PB-208 348

FEASIBILITY STUDIES OF APPLICATIONS OF CATALYTIC OXIDATION IN WASTEWATER

Southern Illinois University
Carbondale, Illinois

November 1971

DISTRIBUTED BY:

NTIS

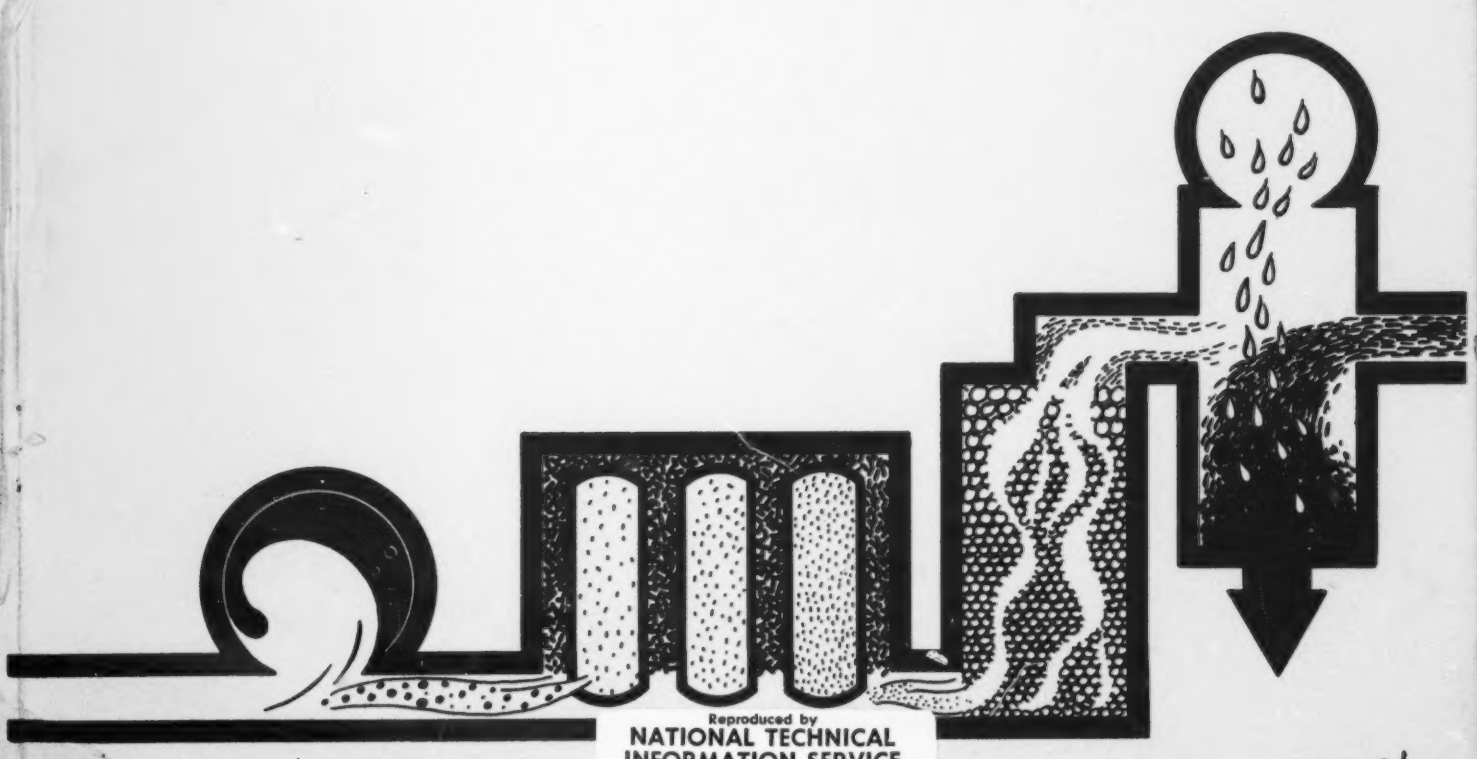
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 208 348

WATER POLLUTION CONTROL RESEARCH SERIES • 17020 ECI 11/71

W72-07103

FEASIBILITY STUDIES OF APPLICATIONS OF CATALYTIC OXIDATION IN WASTEWATER



Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

76

U.S. ENVIRONMENTAL PROTECTION AGENCY

SELECTED WATER RESOURCES ABSTRACTS

INPUT TRANSACTION FORM

1. Report No. | 2. | 3. Accession No. W72-07103

4. Title: FEASIBILITY STUDIES OF APPLICATIONS OF CATALYTIC OXIDATION IN WASTEWATER

5. Report Date

6.

8. Performing Organization Report No.

7. Author(s): [redacted]

10. Project No. Program EPA/ 17020 ECI -- 11/71

9. Organization: Southern Illinois University, Carbondale, [redacted]

11. Contract/Grant No. EPA [redacted]

13. Type of Report and Period Covered

12. Sponsoring Organization: Environmental Protection Agency

15. Supplementary Notes: (Water Pollution Control Research Series [redacted], November 1971, 67 p, 31 fig, 7 tab, 21 ref.

16. Abstract: The recent discovery of the synergistic effects of certain catalysts and ultrasound (sonocatalysis) prompted research investigating the feasibility of using sonocatalysis for advanced wastewater treatment. Sonocatalytic oxidation, sonocatalytic ozonation, and catalytic ozonation were tested individually on treatment plant effluent, and mechanistic studies of sonocatalysis were conducted concurrently using synthetic wastes. Insonation, activated Raney-Nickel catalyst, and air flow produced removals of 78%, 96%, and 100% of COD, Oxygen Demand Index (ODI), and coliforms, respectively, from treated wastewaters. Catalytic ozonation alone was shown to provide 65% COD and 60% TOC removals from treated wastewaters in two hours. Synthetic wastes of phenol and orthochloronitro benzene (OCNB) were prepared and sonocatalytic ozonation of the phenol resulted in a rapid phenol decrease, a less rapid COD decrease and a still slower TOC decrease. The phenol appeared to undergo a step-wise conversion to intermediates at higher oxidation states during slow conversion to carbon dioxide and water. Neither catalytic oxidation nor sono-oxidation of OCNB occurred at room temperature but the sonocatalytic oxidation combination was able to remove all traces of the compound from aqueous solutions. No cost estimate for the process application to secondary effluent was developed. (Lowry-Texas)

17a. Descriptors: *Ultrasonics, *Catalysts, *Ozone, Tertiary treatment, Performance, Optimization, Research and development, Laboratory tests, Analytical techniques, *Oxidation, Phenol, Temperature, *Waste water treatment

17b. Identifiers: *Sonocatalytic oxidation, *Catalytic oxidation, *Catalytic ozonation, Ozonation, Insonation, Nickel

17c. COWRR Field & Group: 05D

Copy available from GPO Sup Doc [redacted], $0.75; microfiche from NTIS as PB 208 348, $0.95.

18. Availability

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price

Send To:

WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Abstractor: Mark V. Lowry | Institution: Texas Univ, Austin

WRSIC 102 (REV. JUNE 1971)

FEASIBILITY STUDIES OF APPLICATIONS OF CATALYTIC OXIDATION IN WASTEWATER

by

SOUTHERN ILLINOIS UNIVERSITY
Carbondale, Illinois

for the

Environmental Protection Agency

Project # 17020 ECI
Contract # 14-12-572

November, 1971

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price 75 cents

EPA Review Notice

This report has been reivewed by the Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

Wastewaters show 78% decrease in Chemical Oxygen Demand (COD) and 96% decrease in Oxygen Demand Index (ODI) during two hours insonation in the presence of activated Raney-Nickel catalyst and air. In addition, sonocatalytic oxidation completely eliminates coliform organisms. The substitution of air by ozone-oxygen mixture can result in COD reductions of 90%. Significantly, treatment with activated Raney-Nickel and ozone, without insonation; i.e., catalytic ozonation; is nearly as effective. This process can remove 85% of the COD and 60% of the TOC from secondary treatment effluents in two hours under favorable conditions.

Ozonation of aqueous phenol solutions in the presence of activated Raney-Nickel and ultrasound (sonocatalytic ozonation) results in the reduction of phenol concentration, COD, and TOC; the greatest decrease is in phenol concentration, the next greatest is in COD, and the least is in TOC.

Aqueous solutions of Orthochloronitrobenzene (OCNB) react only in the presence of ultrasound and aluminum, or activated Raney-Nickel (sonocatalysis) at room temperature. In this reaction, reduction products appear initially, but eventually these products, and OCNB, are eliminated from the solution.

This report was submitted in fulfillment of Project Number 17020 ECI, Contract 14-12-572, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

CONTENTS

	PAGE
Conclusions	1
Recommendations	3
Introduction	5
Literature Review	6
Research Plan	7
Experimental	8
A. Apparatus	8
B. Analytical Procedures	8
C. Experimental Procedures	13
Results and Discussions	14
A. Wastewater Experiments	14
B. Phenol Experiments	36
C. Orthochloronitrobenzene Experiments	58
Acknowledgment	65
List of References	67
List of Publications	69
List of Personnel in the Project	71
Glossary	73

Preceding page blank

FIGURES

		PAGE
1.	Experimental Equipment Schematic	9
2.	Comparison of COD Values Using Standard Method and Technicon COD Analyzer	11
3.	Iodometric Ozone Analysis Apparatus	12
4.	Wet and Dry Weight Ratio of Activated Raney-Nickel in Water	15
5.	COD Reduction Using Ultrasonic Energy	17
6.	Experimental Data Demonstrating the Sonocatalytic Effect	18
7.	Reduction in COD and ODI by Sonocatalysis Using V_2O_5	19
8.	Reduction in COD and ODI by Sonocatalysis Using Activated Raney-Nickel	20
9.	Coliform Reduction by Sonocatalysis Using V_2O_5	22
10.	COD Reduction by Ozonation, Catalytic Ozonation and Sonocatalytic Ozonation	27
11.	ODI Reduction by Ozonation, Catalytic Ozonation and Sonocatalytic Ozonation	28
12.	COD Reduction by Sonocatalytic Ozonation: Effect of Catalyst Dose	29
13.	COD Reduction by Sono-ozonation and Sonocatalytic Ozonation: Influence of Initial COD	30
14.	COD Reduction by Catalytic Ozonation: Effect of Agitation	33
15.	COD Reduction by Catalytic Ozonation: Effect of Catalyst Dose	34
16.	TOC Removal by Catalytic Ozonation	37

17.	Sonocatalytic Oxidation of Phenol	38
18.	Phenol Conversion by Different Oxidative Treatments	40
19.	Catalytic Ozonation of Phenol: Effect of Catalyst Dose	42
20.	Comparison of Phenol Conversion by Oxidative Processes: Effect of Catalyst Dose	43
21.	Conversion of Phenol and COD Removal by Ozonation: Effect of Catalysis by Activated Raney-Nickel	46
22.	Conversion of Phenol and COD Removal by Sono-oxidation: Effect of Catalysis by Activated Raney-Nickel.	47
23.	Conversion of Phenol and COD Removal by Sono-ozonation: Effect of Catalysis by Activated Raney-Nickel	48
24.	Comparison of COD Removal from Aqueous Phenol Solution by Different Types of Treatment	49
25.	TOC Removal in Aqueous Phenol Solution	50
26.	UV Spectra, Sono-ozonation of Phenol (Reference: Water)	52
27.	UV Spectra, Sono-ozonation of Phenol (Reference: Phenol)	53
28.	UV Spectra of Synthetic Mixture and Reaction Products	54
29.	UV Spectra for Different Types of Treatment	55
30.	Thin Layer Chromatograms	56
31.	Structures of Intermediate Products in OCNB Experiments	61

TABLES

		PAGE
1.	A Summary of the Effect of Sonocatalysis on Wastewaters	21
2.	Coliform Versus Time with Ultrasound and Different Catalysts	23
3.	Comparison of Experimental Data of Sonocatalytic Oxidation and Batch Carbon Adsorption	24
4.	Catalytic Oxidation of Wastewater by Boiling	26
5.	Ozone Concentration in Gas Feed Mixtures	32
6.	Ozone Utilization during Ozonation of Wastewater	35
7.	Milligrams Ozone Decomposed and Used in 2-Hour Reaction	44

CONCLUSIONS

1. Sonocatalytic oxidation of wastewaters occurs at room temperature. Insonation, activated Raney-Nickel catalyst, and air flow can remove 78% of the COD, 96% of the ODI, and 100% of coliform organisms in treated wastewaters. As a catalyst, activated Raney-Nickel is stable under ultrasonic irradiation.

2. The replacement of air by ozone-oxygen mixtures (sonocatalytic ozonation) improves the sonocatalytic process.

3. At higher concentrations of ozone, the combination of activated Raney-Nickel and ozone (catalytic ozonation) destroys 85% of the COD and 60% of the TOC in treated wastewaters in two hours under favorable conditions. Catalytic ozonation, as an innovative method for advanced waste treatment, is a significant contribution of this project.

4. There is a sonocatalytic effect observed in the oxidation of aqueous solutions of phenol and orthochloronitrobenzene (OCNB). Sonocatalysis occurs at an optimum dose of catalyst, and greater amounts of catalyst interfere with insonation.

5. Sonocatalytic ozonation of phenol results in a rapid decrease of phenol concentration, a less rapid decrease in COD, and still less rapid decrease in TOC. Phenol appears to be converted in steps to intermediates at higher oxidation states, and is converted, slowly, to carbon dioxide and water. The oxygenated intermediate species identified on the mechanistic pathway are catechol, hydroquinone, pyrogallol, and others.

6. Although neither catalytic oxidation nor sono-oxidation of OCNB occurs at room temperature, the combination of sonocatalytic oxidation does occur which can remove all traces of the compound from aqueous solution. It is possible that insonation dislodges the protective oxide coating from aluminum, exposing fresh metal which is then available for catalytic action.

7. Of the ozone fed into the reaction system, 40% to 75% is consumed during the course of catalytic ozonation and sonocatalytic ozonation.

RECOMMENDATIONS

1. Continue the study of catalytic ozonation as an advanced waste treatment process.

2. Develop a continuous flow reactor for evaluating catalytic ozonation for COD and TOC removal from waste waters.

3. Evaluate ozone consumption and the possibility of ozone recycling.

4. Continue to search for new catalysts comparable to activated Raney-Nickel, investigating catalyst life and regeneration procedures.

5. Continue the study of catalysts and various energy sources to evaluate their synergistic effect.

6. Continue the mechanistic study of catalytic processes with synthetic wastes with the aim of improving the processes with wastewaters.

Preceding page blank

INTRODUCTION

Water pollution has become one of the major problems facing this nation and innovative methods are needed to solve it. Therefore, we decided to embark on a systematic investigation of catalytic oxidation as an advanced wastewater treatment method. Heterogeneous catalytic oxidation is a logical starting point because of the economic advantage in using atmospheric oxygen, and the known capacity of various substances to catalyze the oxidation reaction. Recently, we discovered a synergistic effect between certain catalysts and ultrasound (sonocatalysis). Since waste waters are very dilute solutions of pollutants, and since reactions are usually slow at low concentrations, it seemed appropriate to determine whether sonocatalytic oxidation could increase reaction rates enough to be feasible for wastewater treatment. Aside from a consideration of reaction rates, there was evidence that sonocatalysis could destroy pollutants which neither catalytic oxidation, nor ultrasound, could accomplish alone. The objective of this research, therefore, is to investigate the feasibility of using catalytic and sonocatalytic processes for advanced wastewater treatment.

The experimental approach consisted of four parts:

(1) Sonocatalytic oxidation (ultrasound + catalyst + environmental oxygen) as a treatment process for wastewater and for representative compounds.

(2) Sonocatalytic ozonation (ultrasound + catalyst + ozone) as a treatment process for wastewater and for representative compounds.

(3) Catalytic ozonation (catalyst + ozone) as a treatment process for wastewaters and for representative compounds.

(4) Mechanistic studies of sonocatalysis in synthetic wastes.

To evaluate the effectiveness of these processes for wastewater treatment, it is desirable to use the effluent from a sewage treatment plant for experimentation. This furnishes a direct means to test and compare the efficiency of the process with the existing one. On the other hand, constituents of waste waters cannot be held constant and assays are not available for making detailed analyses. It is not possible to interpret the data accurately for a kinetic study. Therefore, a synthetic waste or a representative compound should be used in order to investigate the mechanism of catalytic reactions, and to determine their interactions

Preceding page blank

with ultrasonic energy. Both phenol and orthochloronitrobenzene (OCNB) are important and common aromatic compounds in industrial wastes. OCNB is difficult to remove by biological processes. Therefore, the choice of these two compounds for a mechanistic study would be of both practical and theoretical value.

LITERATURE REVIEW

Weissler (16) did an extensive study on the iodine clock reaction under ultrasonic irradiation at high frequency (400 KHz and 1000 KHz). It was found that the reaction rates were influenced by the variation of sound intensity, duration of exposure, and the presence of a particular gas.

Chen and Kalback (2) studied the effect of sonic vibrations on the hydrolysis of methyl acetate using a low frequency (23 KHz) generator. They found that the reaction rate increases with an increase of ultrasonic intensity. However, Fogler and Barnes (7) studied the optimum ultrasonic power of the same reaction at 27.5 KHz and concluded that the rate of reaction does not increase indefinitely with increasing intensity. Instead, it reaches some optimum value after which any further increase in power input only decreases the reaction rate.

Polotskii (13) reported the action of ultrasonic irradiation at high frequency on certain aqueous solutions produced both nitrate and nitrite compounds. Fitzgerald (6) conducted a series of experiments on insonation of distilled water saturated with various gases to produce hydrogen peroxide in aqueous environment.

Lur'e (11) did an extensive study on the oxidation of potassium iodide and aqueous phenol solutions in an ultrasonic field at high frequency (800 KHz). He found that the oxidation reaction in an ultrasonic field is due to ionization of water molecules and the formation of reactive free radicals. These radicals may enter into the benzene ring and decompose the phenol molecules.

The ultrasonic cleavage of certain heterocyclic and aromatic rings to produce acetylene has been reported by Zechmeister and his collaborators (17,18). A similar result has also been observed by Currell and Zechmeister (4) in the ultrasonic treatment of aqueous solutions of cyclohexanol.

Jellinek and Whitte (8) conducted a series of experiments on the degradation of long chain molecules by ultrasonic waves. They reported that ultrasonic degradation of long chain molecules in solution under ordinary conditions is intimately connected with

the collapse of small cavities. During such a collapse, velocity and pressure gradients are generated in the neighborhood of the cavity.

Heterogeneous catalysts, both metals and metal oxides, have been used (4) in the catalytic oxidation of carbon monoxide, sulfur dioxide, ammonia, methanol and hydrocarbons such as aliphatic, aromatic and heterocyclic compounds at elevated temperatures. No information is known in the literature for catalytic oxidation in aqueous solution at ambient temperatures except the previous work by Chen, Chang and Smith (3).

Ozone has been used for many years in various European cities for the purification of water (15). The city of Philadelphia in Pennsylvania has used this method (1). Ozone is generally reported to be very effective for disinfection and to decrease odors, tastes, and organic matter of waters.

Ozone is about 13 times more soluble in water than oxygen. The solubility of pure ozone is reported to be between 0.57 and 0.8 g/l at 20°C. At saturation, an aqueous solution in contact with oxygen containing 2 wt. percent ozone will contain about 11 mg/l ozone and 40 mg/l oxygen (9,10).

Processes have been developed for the destruction of oxidizable waste in industrial waters. For example, ozone has been shown to be effective in destroying phenols (12) and cyanides (14). Aromatic compounds are oxidized with formation of ozonides and eventual decomposition of the ring structure.

RESEARCH PLAN

The research plan of the present project includes the following considerations:

1. Set up a reaction system which can be used to evaluate sonocatalytic oxidation, sonocatalytic ozonation and catalytic ozonation processes for wastewater treatment.

2. Evaluate the performance of each process using the effluents from Carbondale sewage plants, and pure solutions of phenol and OCNB.

3. Investigate the significance of parameters of the processes such as ultrasonic intensity, amount of catalyst, reaction time, gas flow rate, ozone consumption, initial pollutant content in the waste waters, and the stability of the catalysts.

4. Obtain kinetic information with wastewaters as well as with synthetic wastes.

5. Study the mechanisms involved in sonocatalysis.

EXPERIMENTAL

A. Apparatus

The experimental equipment is shown schematically in Figure 1. A thin-walled, flat bottomed pyrex tube (2.25 in. x 16 in.) was used as a reaction vessel. Inside the vessel, two 2-mm I.D. glass tubes extending from the upper part of the vessel to the bottom allowed for sparging gas into the solutions. A condenser was connected to the top of the vessel by 60/50 and 24/40 joints for condensing the mist produced by ultrasonic vibrations. The vessel was immersed in a constant temperature jacket.

A section of plexiglass tubing, 6-inches O.D. by 12-inches long, was used as a constant temperature jacket. Constant temperature water was circulating into the jacket through a 1/4 inch water tap 1 inch from the bottom of the jacket and drained out by gravity through a 1/2-inch water tap located 2 inches from the top of the jacket. The temperature of circulating water was maintained within ±0.5°C of the predetermined temperature.

The 800 KHz Macrosonic submersible piezoceramic transducer with a surface area of 1.5 square inches was mounted at the center of the bottom of the jacket. A Macrosonics Model 180-VF high frequency generator supplied power to the transducer.

A scale was attached on the front wall of the jacket to ensure accurate placement of the reaction vessel one inch above the transducer surface. The same reaction vessel was used throughout this research to eliminate the effect of wall thickness.

For studies of catalytic processes, the same reaction system was used. Instead of using ultrasonic irradiation to homogenize the reaction mixture, a magnetic stirrer was used for agitation.

Two ozonators were used to generate ozone. A Welsbach Model T23 ozonator produces about 68 mg ozone per hour at 1.15 mg/l. The other one, Welsbach Model T408, generates about 10 g ozone per hour at about 33 mg/l.

B. Analytical Procedures

1. Chemical Oxygen Demand (COD) - The standard dichromate procedure is given in Reference (19). In all analyses, 50-ml

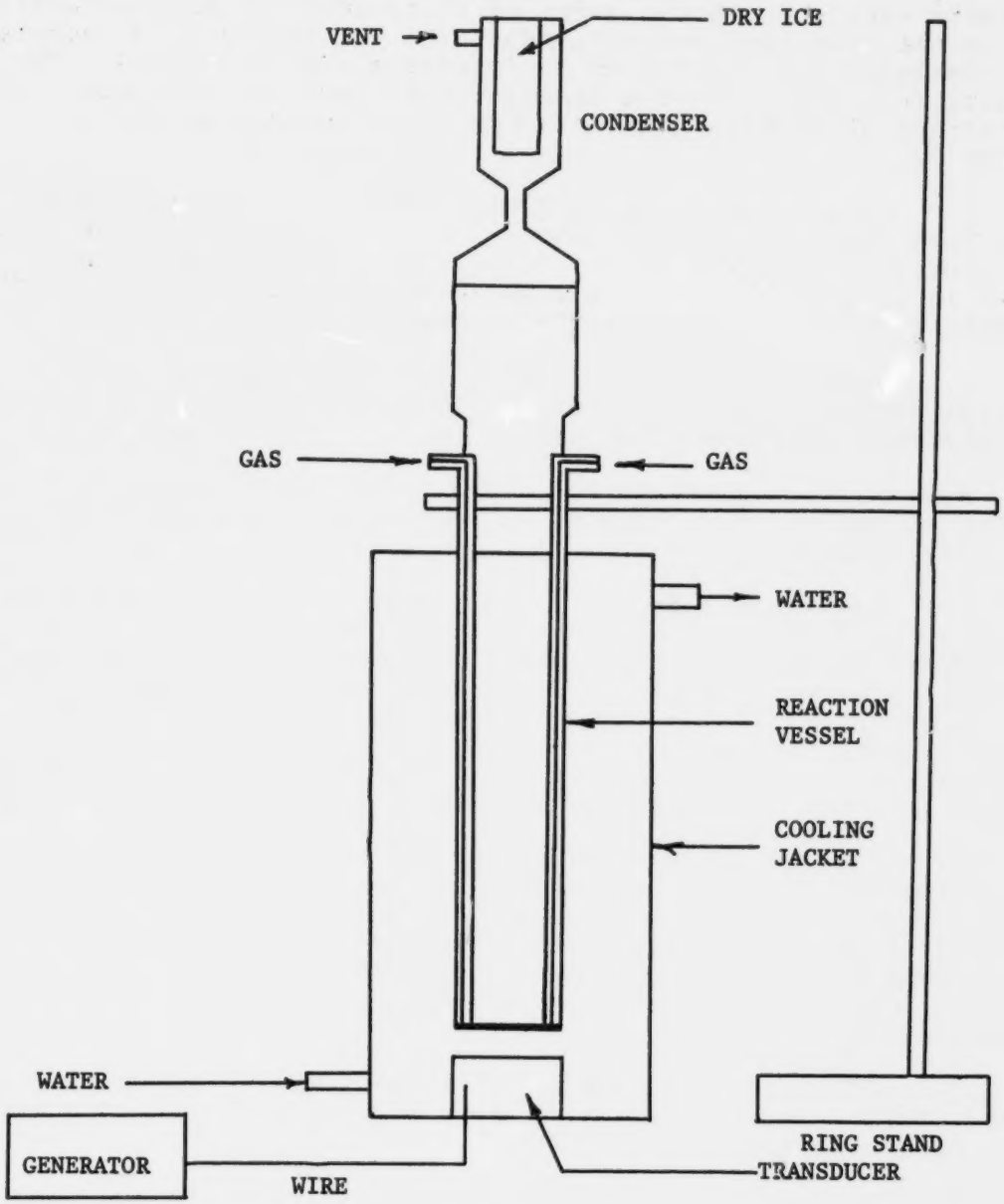


Figure 1: Experimental Equipment Schematic

aliquots were used. Silver sulfate and mercuric sulfate were added to each sample to catalyze organic oxidation and prevent chloride interference, respectively. According to Standard Methods, the accuracy of the COD test for most organic compounds in waste waters is on the order of 95 to 100% of the theoretical. Due to the time required to conduct the wet analysis, a Technicon Auto-Analyzer was later used to determine COD in samples. The results from the Technicon Analyzer were very satisfactory. A comparison of experimental data from these methods is shown in Figure 2.

2. Oxygen Demand Index (ODI) - Model Dr. Colorimeters from Hach Chemical Company (Ames, Iowa) is used to analyze ODI. The procedure is given in Reference (20). The Oxygen Demand Index is a rapid chemical test which gives an approximate of the normal five day Biochemical Oxygen Demand (BOD).

3. Coliform Analysis - Sabro Coliform Analyzer from General Ionics Corporation (Bridgeville, Pennsylvania) was used to determine coliform organisms.

4. Total Organic Carbon (TOC) - The total amount of organic carbon in the reaction samples was determined by a Beckman Model 915 Total Carbon Analyzer.

5. Gas Chromotography - The phenol concentration in the samples was determined by gas chromotographic analysis. A 5' x 1/8" OV-17 column (5% methyl-phenyl-silicone on 80/100 mesh chromosorb W) was used in a Varian Aerograph Model 1520C Gas Chromotograph. The Gas Chromotograph has a flame ionization detector with nitrogen as the carrier gas. The temperature conditions were: Column 150°C, injector 190°C and detector 210°C. Sample size for injection was usually 1.5 µl.

6. Thin Layer Chromotography (TLC) - In attempting to determine the reaction products, thin layer chromotography was used. For the thin layer material, a 2:3 mixture of Silica Gel HF - 254 + 366 and Silical Gel G was used. The developing solvents were mixtures of cyclohexane and ethyl acetate in different ratios. Some IR, NMR and Mass-Spectra were run on the compounds separated on TLC.

7. UV Spectrophotometry - For the identification of compounds formed during treatment, some spectra were run on a Beckman UV - Spectrophotometer Model DB.

8. Determination of Ozone Concentration - The equipment for the absorption of ozone for measurement is shown in Figure 3. The ozone-oxygen mixtures from the outlet of the ozonator were passed through a fritted-glass sparger in a gas absorber containing

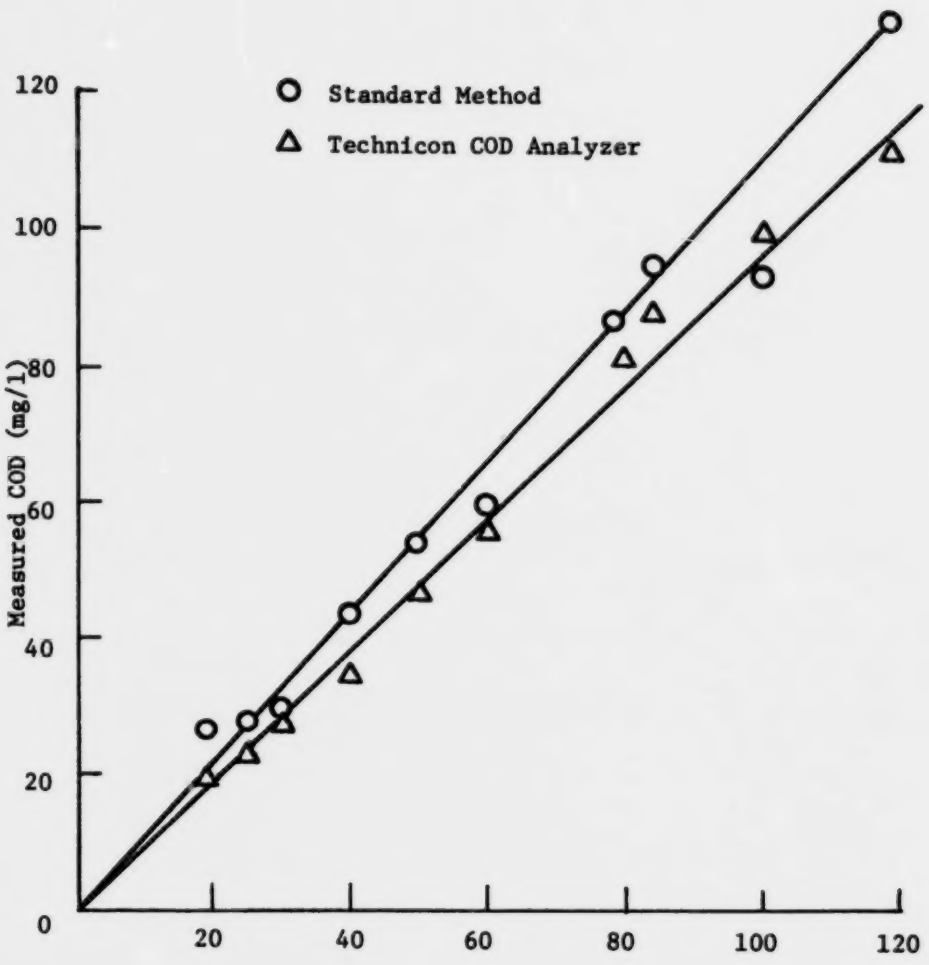


Figure 2: Comparison of COD Values Using Standard Method and Technicon COD Analyzer

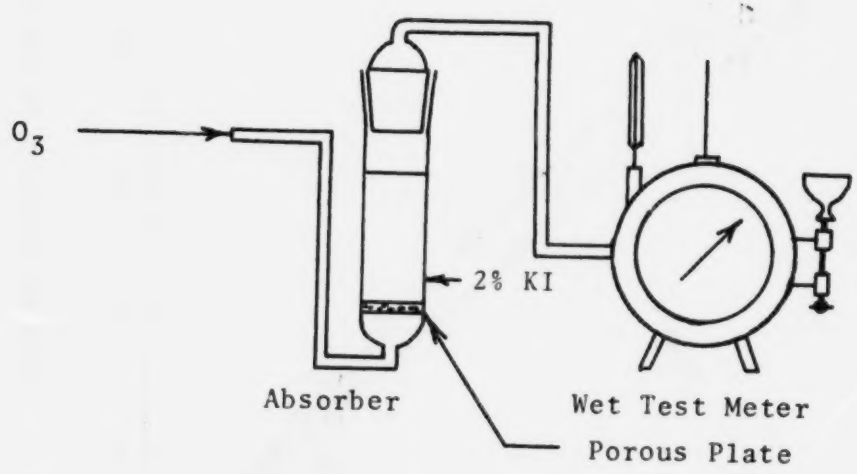


Figure 3: Iodometric Ozone Analysis Apparatus

400 ml of 2% KI solution. The volume of gas was measured by a wet test meter. Ten ml of 10% sulfuric acid and 10 ml of starch indicator were added to KI solution after absorption, and the iodine produced was titrated with standard 0.1 N thiosulfate solution. The ozone concentration (C) is calculated according to the following equation:

$$C = \frac{(\text{Normality of } Na_2S_2O_3)(\text{Volume of } Na_2S_2O_3)}{(\text{Corrected sample volume in liters})} \quad (24)$$

C = Concentration of ozone in mg/l.

The amount of dissolved ozone used in reaction and decomposed in the reaction solutions was determined by sparging the feed gas mixture into waste waters and measuring the difference in ozone concentration between theinlet gas and the effluent gas (21).

9. Ultrasonic Intensity Measurement - To determine the ultrasonic intensity applied to the reaction mixture, 350 and 3250 milliliters of water were placed in the reaction vessel and in the cooling jacket, respectively. Ultrasound of a known level was applied to the stationary water for a measured period of time. The temperature change of the water in both the reaction vessel and in the cooling jacket was measured.

From the temperature rise, the power input was evaluated for each ultrasonic intensity level.

C. Experimental Procedures

In the wastewater experiments, effluent samples from the Carbondale city sewage treatment plant were used. Secondary effluent from an activated sludge process was stabilized in a refrigerator for three to five days, and the solid precipitants filtered out before the experiments were conducted.

In all of the experiments, 350 ml of reaction mixture (waste waters or synthetic waste), with or without catalyst, was charged into the reactor (Figure 1). Compressed air or ozone-oxygen mixture was sparged into the reaction mixture slowly through a rotameter.

In a typical sonocatalytic experimental run, the reactor vessel was placed in the cooling jacket and the bottom of the reactor was carefully adjusted to a distance of one inch above the transducer surface. After proper adjustment, a known amount of reaction mixture and catalyst were put into the reactor, and the ultrasonic generator was then switched on.

Aliquots of the reactor mixture were withdrawn at different time intervals for analysis. The samples with catalysts in them were centrifuged and filtered to obtain clear solutions before

the analysis was performed.

Activated Raney-Nickel from Davison Division of W. R. Grace and Company (South Pittsburg, Tennessee) was stored in water. A series of experiments were conducted by weighing the wet and dry Raney-Nickel; the data are shown in Figure 4. From the plot, the dry weight of the activated Raney-Nickel can be estimated.

In the experiments without ultrasonic irradiation, a magnetic stirrer was used to agitate the reaction mixture. All other experimental procedures were identical to those of the sonocatalytic ones.

RESULTS AND DISCUSSION

The results and discussions of this report are divided into three parts. They are:

A. Wastewater Experiments
B. Phenol Experiments
C. Orthochloronitrobenzene Experiments

In the wastewater experiments, the effort was concentrated on investigating the feasibility of different processes for advanced waste treatment. Their performances were evaluted at various operating conditions. The results were empirical in nature.

In the phenol study, both empirical and kinetic information were obtained. An attempt was made to investigate the mechanisms involved in the sonocatalytic processes.

The work on orthochloronitrobenzene was primarily a mechanistic investigation. Some experiments were also performed to show the feasibility of eliminating the compound from waste waters.

A. Wastewater Experiments

Three sets of experiments were conducted for wastewater: sonocatalytic oxidation, sonocatalytic ozonation and catalytic ozonation.

1. Sonocatalytic Oxidation

In the sonocatalytic oxidation work, 350 ml of wastewater was used, and the experimental procedure, previously described, was followed.

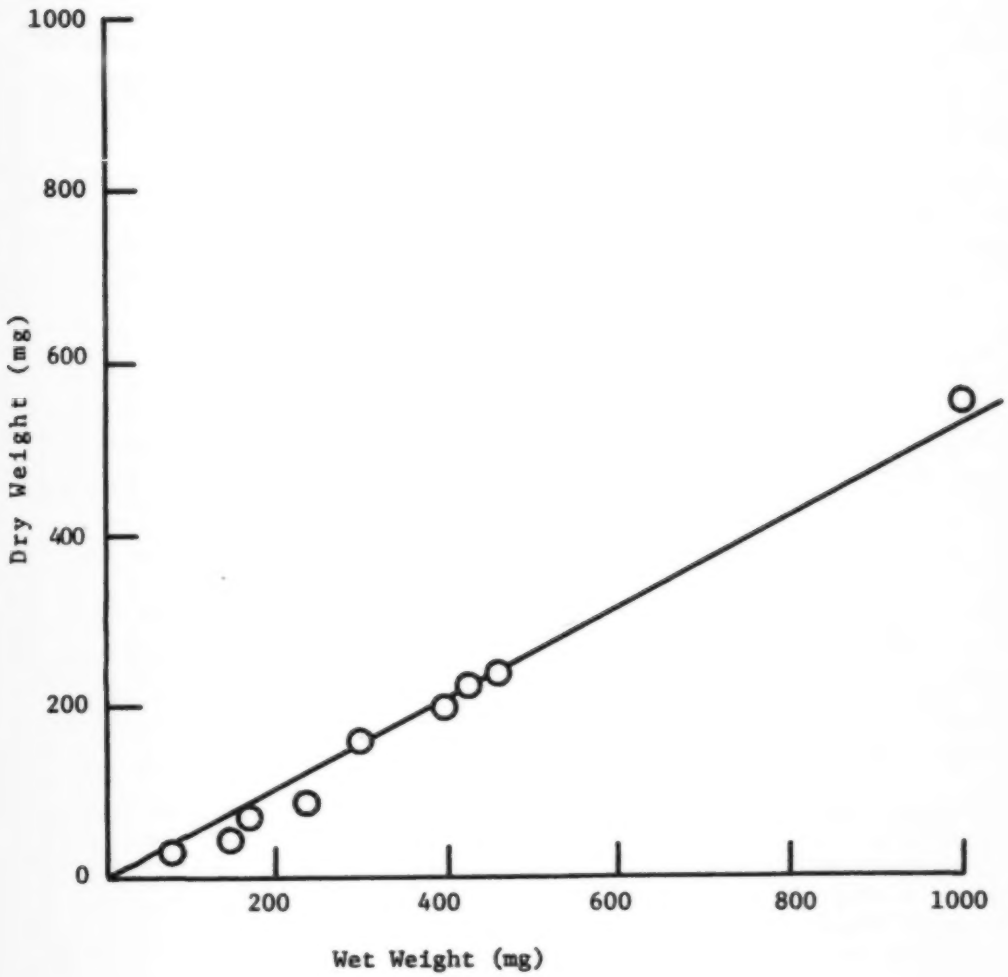


Figure 4: Wet and Dry Weight Ratio of Activated Raney-Nickel in Water

Figure 5 shows COD reduction in wastewaters by ultrasonic energy at two levels of ultrasonic intensities. It can be seen that at a frequency of 800 KHz, the rate of COD removal increased due to irradiation with ultrasonic energy. However, increasing the energy level above 18.2 watts/cm^2 did not improve significantly the COD removal rate.

Experimental results shown in Figure 6 are a demonstration of the sonocatalytic effect. Using a reaction mixture containing twenty milligrams of MnO_2 catalyst in 350 ml of wastewater, sonocatalytic oxidation is more effective for COD reduction than either catalysis or ultrasonic irradiation alone. The effect of the sonocatalytic reaction is greater than the additive effects, and a synergistic behavior is observed.

Figures 7 and 8 show the reduction in the COD and ODI in wastewater by sonocatalytic oxidation using V_2O_5 and activated Raney-Nickel, respectively. It appears that both catalysts can effectively destroy the pollutants in wastewater. However, the V_2O_5 catalyst is not physically stable under ultrasonic treatment; the catalyst is solubilized and the wastewater becomes yellow during the course of sono-reaction. On the other hand, activated Raney-Nickel catalysts were very stable during ultrasonic irradiation. No breakage of the catalyst was observed, and the color of the wastewater remained clear. A summary of the experimental results using various catalysts is listed in Table 1. Of the wide assortment of catalysts used, activated Raney-Nickel catalyst was most effective for the removal of COD and ODI from wastewater.

It is shown in Figure 9 that substantial reduction in coliform organisms can be obtained by sonocatalytic oxidation using V_2O_5 as catalyst. However, it was concluded from similar studies using other catalysts, and ultrasound alone, that essentially complete kills can also be achieved by ultrasonic radiation alone (Table 2).

It was interesting to compare sonocatalytic oxidation with the well-known carbon adsorption process. T.M. Granular activated carbon from Calgon Corporation was used for experimentation. The experimental data are shown in Table 3. It can be seen that sonocatalytic oxidation with activated Raney-Nickel catalyst is compared favorably with batch carbon adsorption.

As one of the possible explanations for the sonocatalytic effect, it was thought that ultrasonic energy generates heat on the surface of the solid catalysts, and that the high surface temperature would promote the reaction. If this were true, then a similar effect could be obtained simply by boiling the reaction mixture with the catalyst at high temperature.

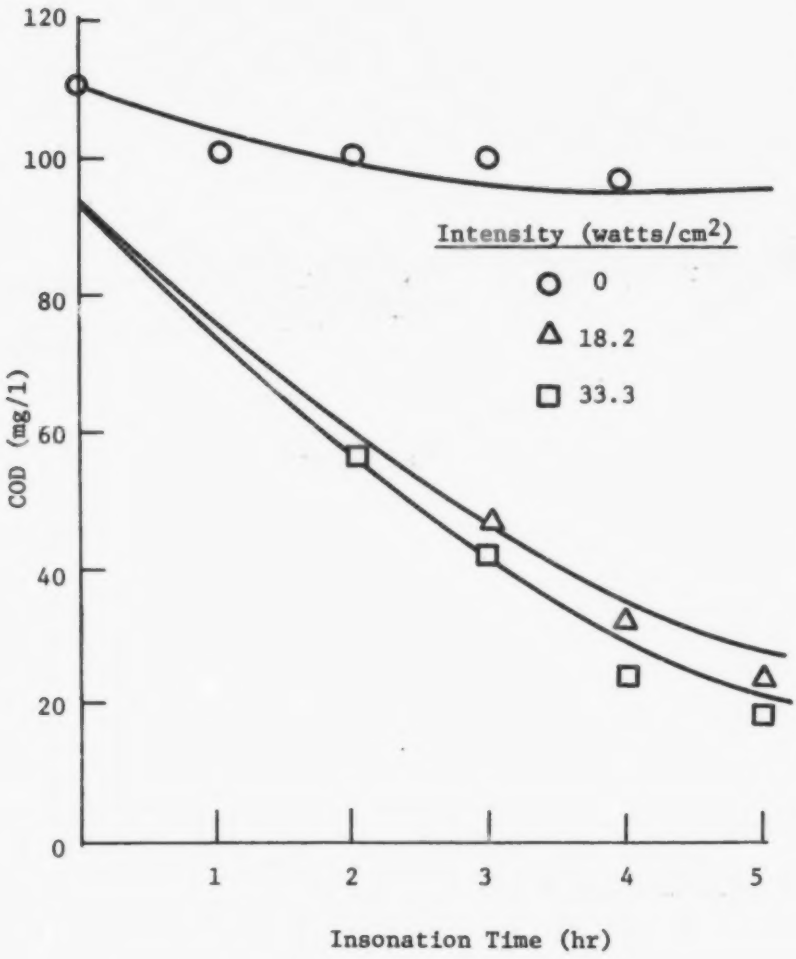


Figure 5: COD Reduction Using Ultrasonic Energy: Effect of Ultrasonic Intensity at 800 KHz and 25.5°C

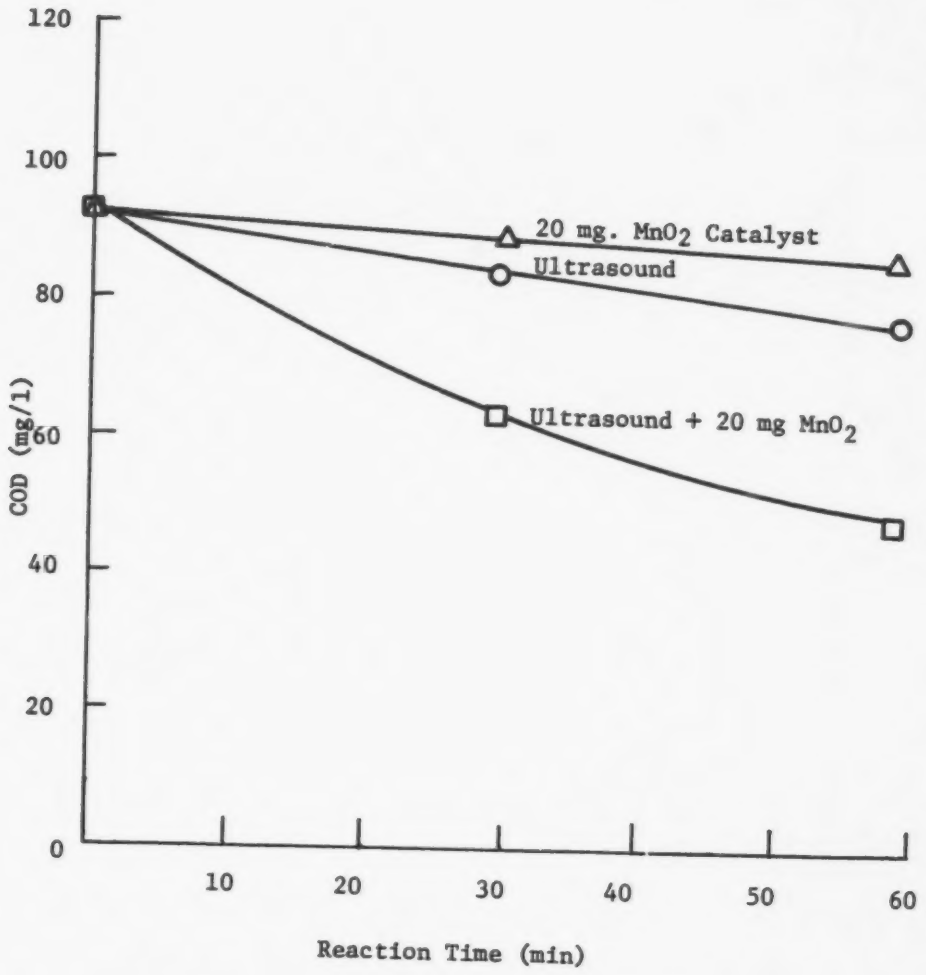


Figure 6: Experimental Data Demonstrating the Sonocatalytic Effect

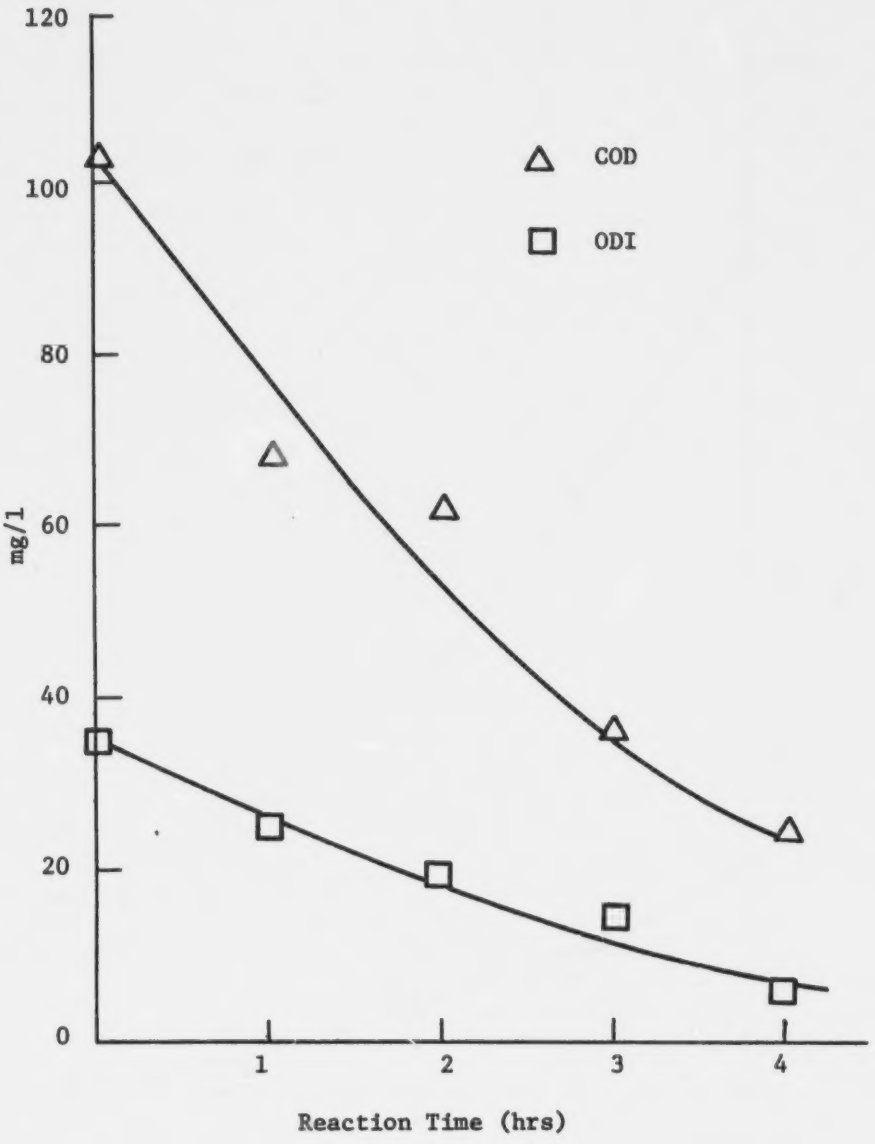


Figure 7: Reduction in COD and ODI by Sonocatalysis Using V_2O_5

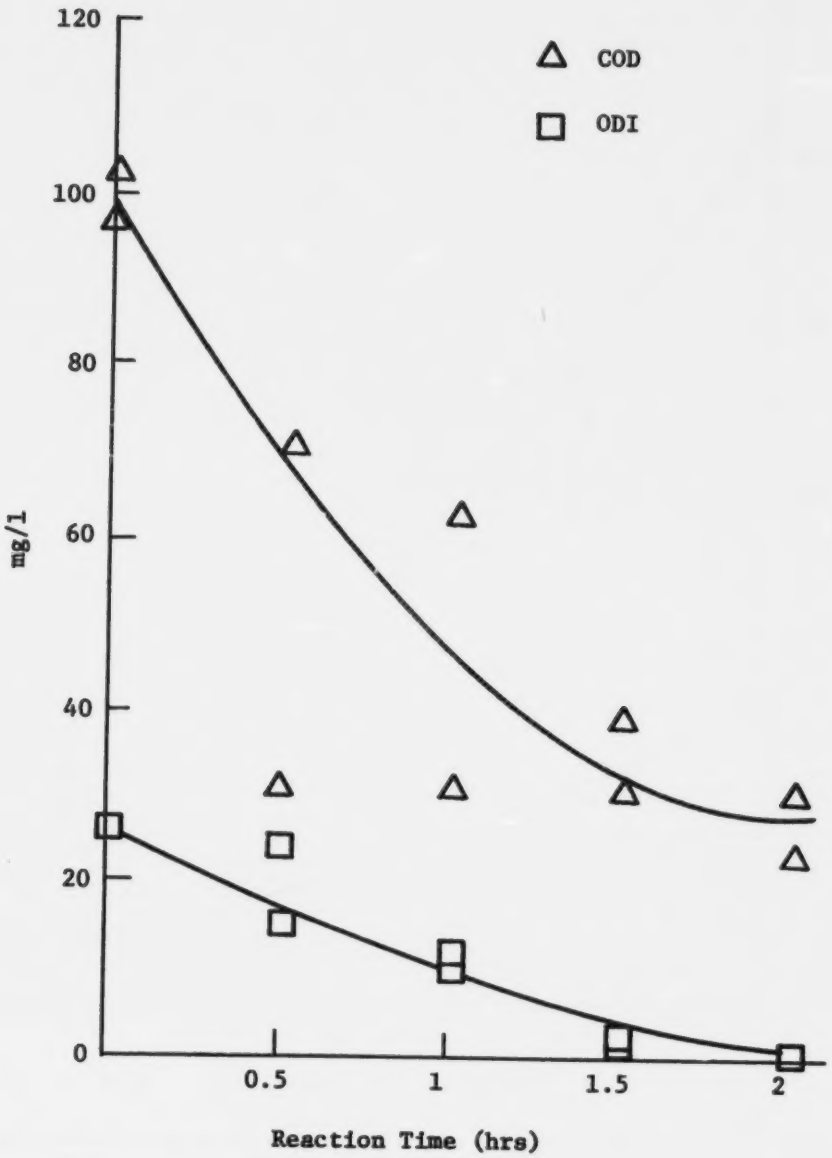


Figure 8: Reduction in COD and ODI by Sonocatalysis Using Activated Raney-Nickel

TABLE 1: A SUMMARY OF THE EFFECT OF SONOCATALYSIS ON WASTEWATER

	Amt. (mg/ 350 ml of Wastewater)	Ultrasonic Energy (watts/cm^2)	% COD Reduction in 2 Hours	% ODI Reduction in 2 Hours	Stability of Catalysis Under Ultrasonic
Ni Supported on Kieselguhr	500	33.3	40%	48%	Stable
MoO_3 Supported on Alumina	500	33.3	49%	56%	Stable
ZnO Supported on Alumina	500	33.3	39.5%	33%	Stable
Activated Raney Nickel	1000	33.3	78%	96%	Stable
V_2O_5	20	33.3	42%	45%	Soluble in Water
Pt. Black	20	33.3	48%	47%	Stable
Al_2O_3	20	33.3	35%	52%	Became Colloidal
FeO_3	20	33.3	7%	20%	Became Colloidal
Silica Gel	500	33.3	63%	68%	Particals Broken Up
Silica Gel	500	0	38%	30%	Stable
MnO_2*	20	33.3	50%*		Became Colloidal
MnO_2*	20	0	9%		Stable
None*	0	33.3	18%		

*Experimental Data at One Hour

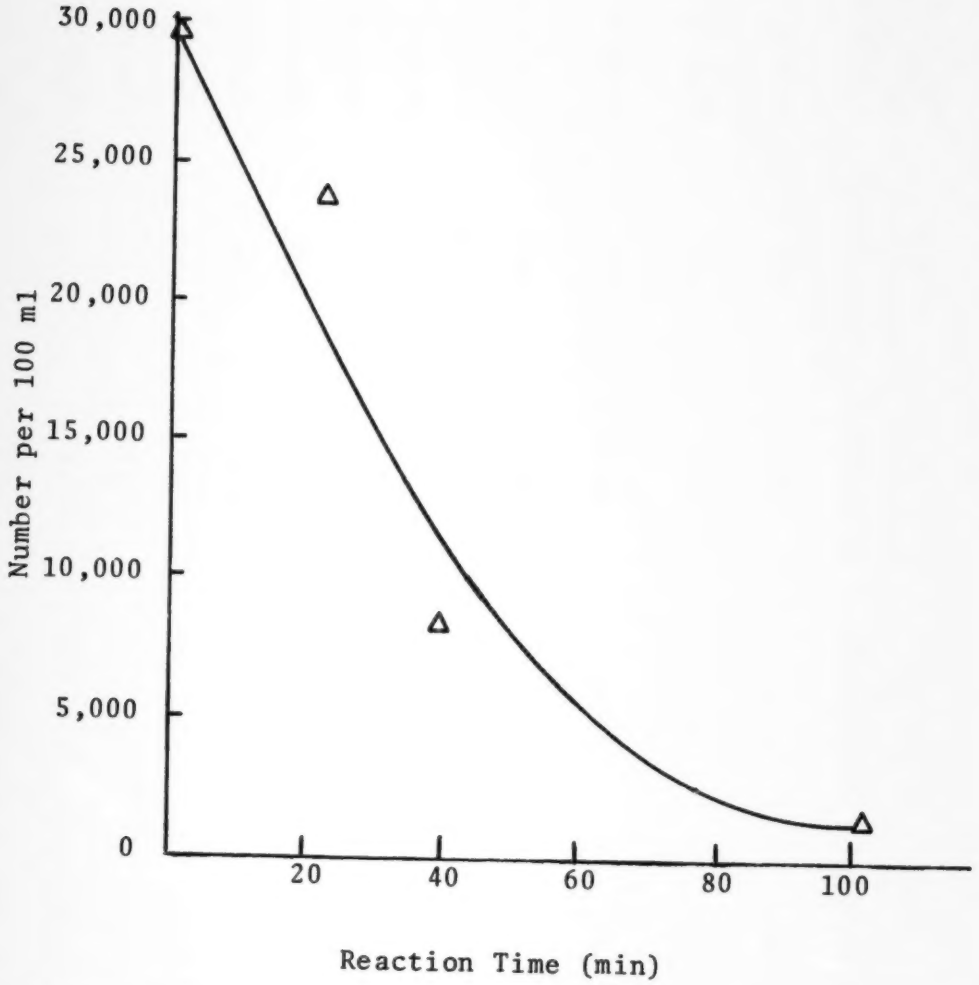


Figure 9: Coliform Reduction by Sonocatalysis Using V_2O_5

TABLE 2: Coliform versus time with different catalysts (20 mg in 350 ml waste waters), at 25.5°C, ultrasonic treatment intensity 33.3 watts/cm^2, air flow.

CATALYST	ULTRASOUND	COLIFORM (ORIGINAL)	COLIFORM (4 hr)
MnO_2	yes	31500	0
PtO_2	yes	22300	0
Ag_2O	yes	20600	0
V_2O_5	yes	28800	0
V_2O_5	no	20100	3900
no	yes	26200	0

TABLE 3: Comparison of the experimental data of sonocatalytic oxidation with activated granular carbon adsorption on reduction of ODI in waste waters (initial ODI concentration 25 ppm).

Item / AMOUNT	ONE HOUR		TWO HOURS	
	RANEY-NICKEL WITH ULTRASONIC TREATMENT	ACTIVATED GRANULAR CARBON	RANEY-NICKEL WITH ULTRASONIC TREATMENT	ACTIVATED GRANULAR CARBON
70 mg	23	22	20	20
200 mg	21	22	18	16
500 mg	18	19	13	13
1000 mg	10	15	0	9

To test this hypothesis for wastewater samples, three experiments were conducted. The experimental data are given in Table 4. It can be seen that heat generated by boiling effects negligible changes in COD and ODI.

2. Sonocatalytic Ozonation

After it was determined from the sonocatalytic oxidation experiments that activated Raney-Nickel was the most suitable catalyst from the standpoint of stability and effectiveness, an attempt was made to improve treatment efficiency by using ozone-oxygen mixture as the gas flow. A set of experiments were conducted to investigate the ozonation of wastewater under the following conditions:

a. Ozonation alone
b. Ozonation and activated Raney-Nickel catalysis
c. Ozonation and ultrasonic irradiation
d. Ozonation, catalysis, and ultrasonic irradiation.

A Welsbach Ozonator Model T23 was used initially to generate ozone. The rate of ozone generated was very small; only 68 mg per hour.

The effectiveness of each method of treatment in reducing the COD, and ODI, of wastewater is shown in Figures 10 and 11, respectively. The results indicate that sonocatalytic ozonation (condition d., above) gives the best performance. The fact that the effectiveness of ozone oxidation can be improved by catalysis suggests the possibility of a new process which can find application in waste treatment. Even greater efficiencies could be realized by optimization techniques.

The effect of various doses of activated Raney-Nickel catalyst on sonocatalytic ozonation is presented in Figure 12. It is shown that large increases in the catalyst dose results in only a minimal increase in the rate of COD removal in wastewater, within the range investigated.

The effect of initial concentration of COD in wastewaters on the rate of COD removal at 25.5°C and 33.3 watts/cm^2 is presented in Figure 13. Wastewater samples with a lower COD value were obtained by passing the effluent from the secondary treatment plant through a carbon adsorption column. In this way, the COD of the effluent was reduced from an initial value of 100 mg/1 to 42 mg/1 and 12 mg/1. Each sample was treated under identical experimental conditions. As seen in Figure 13, the greatest COD removal is obtained when the initial COD is highest. Also, after 2 hours reaction time, the greatest COD remains in the sample which had the greatest initial COD. In other words, the final COD is directly

TABLE 4: Catalytic Oxidation of Wastewater by Boiling

Item / Time	COD			ODI		
	Raney Nickel 500 mg	Raney Nickel 500 mg Zeolite 500 mg	Zeolite 500 mg	Raney Nickel 500 mg	Raney Nickel 500 mg Zeolite 500 mg	Zeolite 500 mg
Initial concentration	74	74	74	26	26	26
Two hour boiling	68	70	71	22	25	25

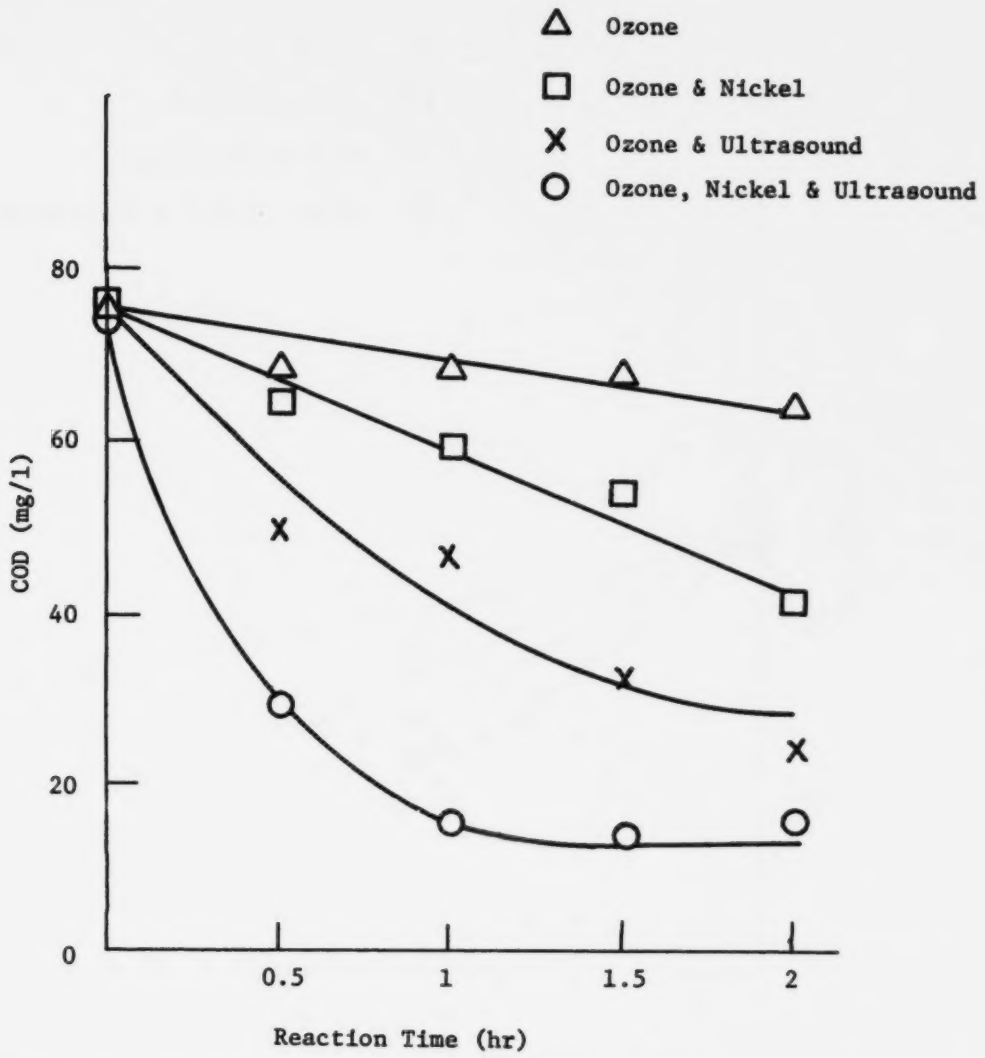


Figure 10: COD Reduction by Ozonation, Catalytic Ozonation, and Sonocatalytic Ozonation

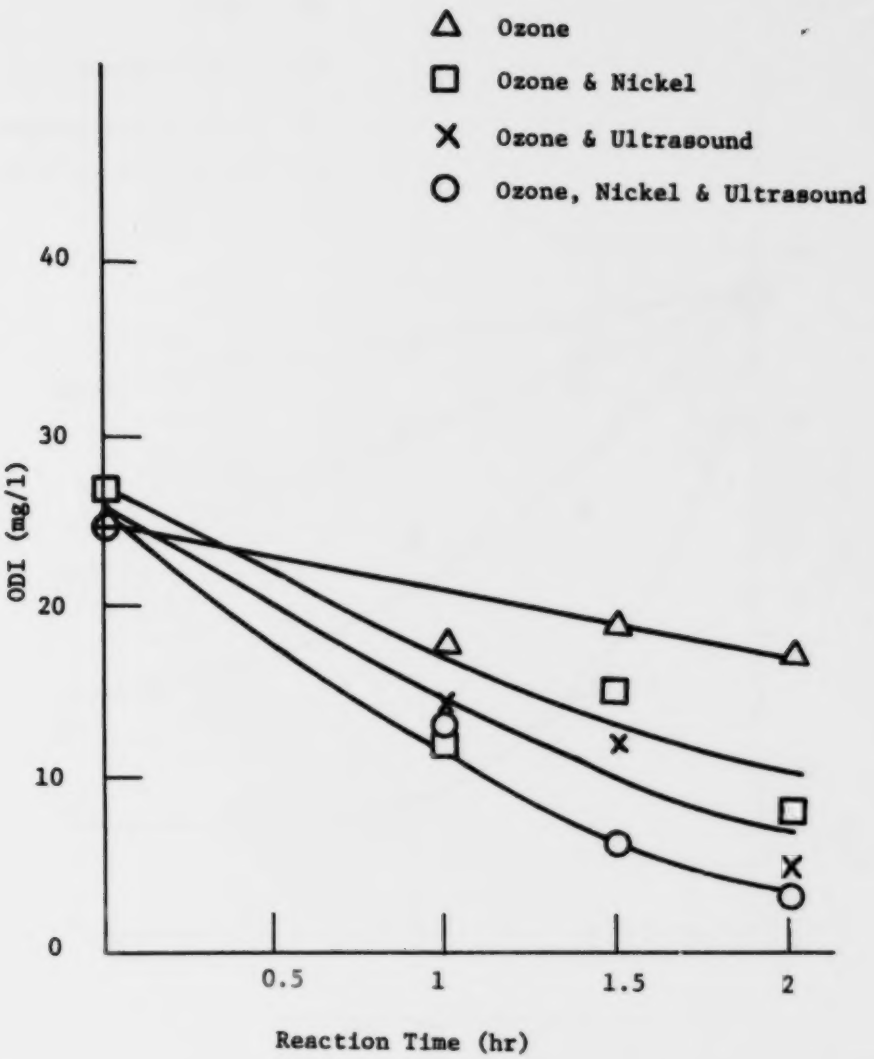


Figure 11: ODI Reduction by Ozonation, Catalytic Ozonation, and Sonocatalytic Ozonation

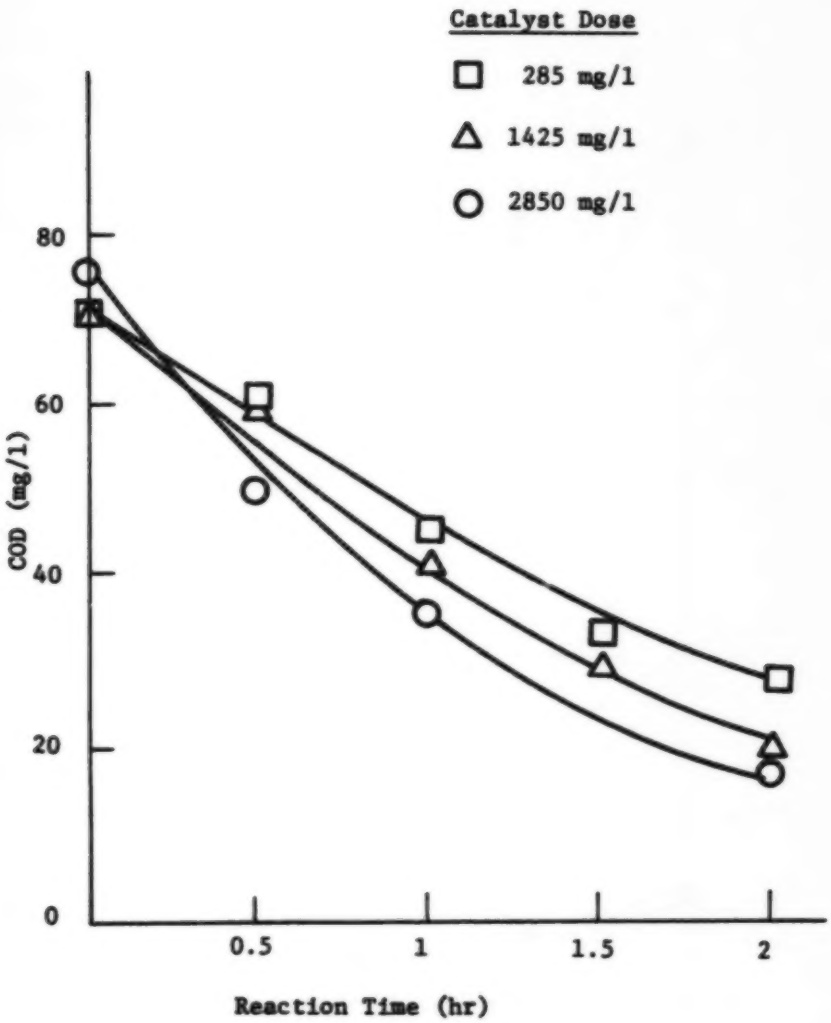


Figure 12: COD Reduction by Sonocatalytic Ozonation: Effect of Catalyst Dose

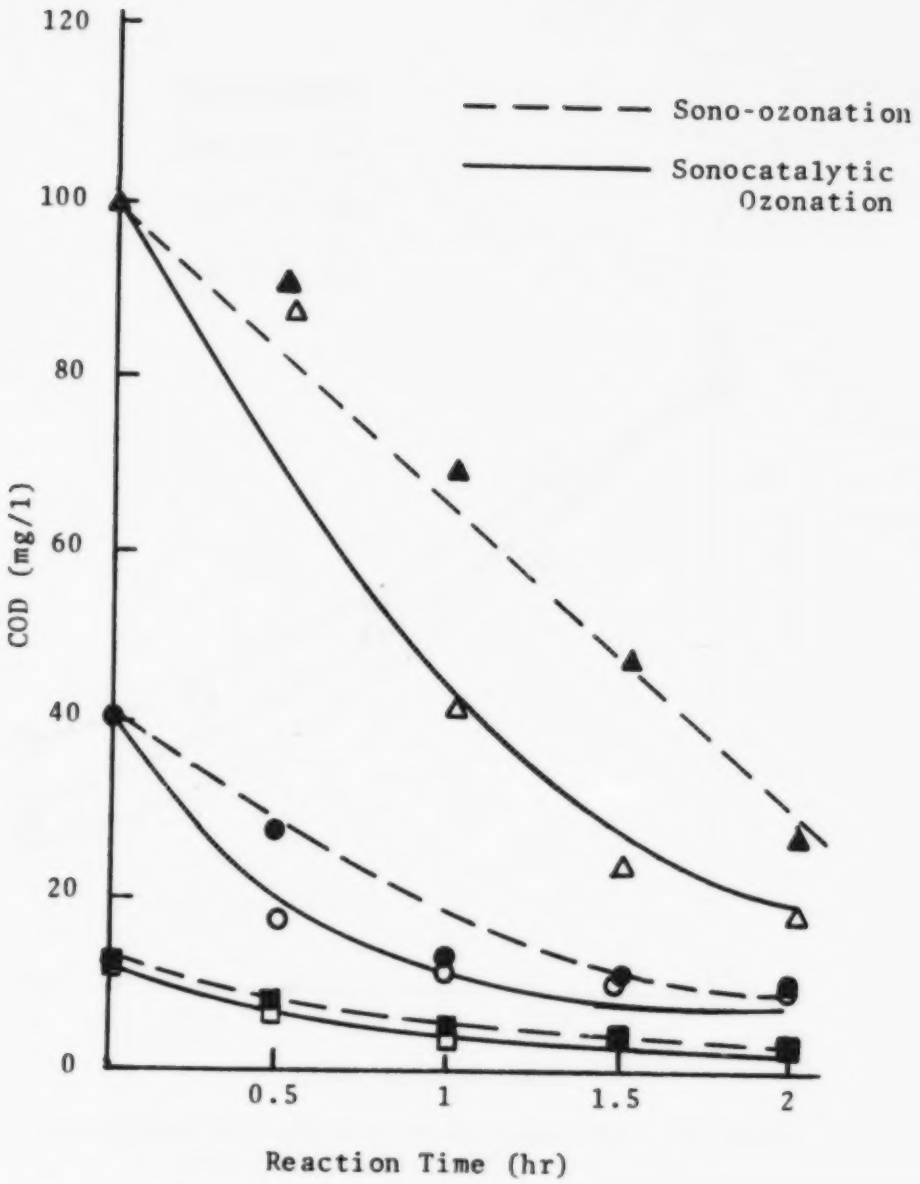


Figure 13: COD Reduction by Sono-ozonation and Sonocatalytic Ozonation: Influence of Initial COD

related to initial COD; the percent removal being about the same for each of the three samples (about 75%).

3. Catalytic Ozonation

The experimental results for COD removal by catalyzed ozonation reactions (Figure 10) indicated that catalytic ozonation (as well as sonocatalytic ozonation) could be a potential treatment process for wastewater. Catalytic ozonation will be further considered in this section.

In previous experiments, the ozonator used produced only a small amount of ozone (about 68 mg of ozone per hour at 1.15 mg/l of ozone). Since further experimentation of this process seemed desirable, a new ozonator of greater capacity was purchased. The ozone concentrations in the gaseous mixtures at different flow rates from this generator were determined by the iodometric method. The data are shown in Table 5. It can be seen that about ten grams of ozone per hour at 33.0 mg/l were generated by this ozonator. (This is compared to 68 mg of ozone per hour generated by the previously used ozonator.)

Figure 14 shows data from four experiments in catalytic ozonation. In two of those experiments, agitation in the reaction mixture was accomplished by ozone bubbling alone. A magnetic stirrer was used to agitate the reaction mixture in the two other experiments. The results indicated that the type of agitation did effect the oxidation rate and, therefore, a magnetic stirrer was used in subsequent runs.

Experimental results for catalytic ozonation using samples at different initial COD levels and different amounts of catalyst are presented in Figure 15. It is seen that within the catalyst range studied, the rate of COD removal is increased with an increase in the amount of catalyst used; and that a lower COD results when the initial COD is lower. The removal of up to 85% of the COD from strong effluents, and up to 80% from a better quality sample suggests that catalytic ozonation could be applied under a variety of circumstances in wastewater treatment.

In order to determine the amount of ozone consumed during the catalytic ozonation process, the concentration of ozone in the gas mixture was measured at the inlet and the outlet of the reaction system. The data in Table 6 indicate that greater agitation; i.e., mixing versus simple bubbling; results in greater amounts of ozone used in reaction, which agrees with the COD data shown previously in Figure 14. High-shear mixing would, no doubt, result in increased rates of ozone utilization and increased rates of COD removals.

TABLE 5: Ozone Concentration in Gas Feed Mixtures

SAMPLE	GAS FLOW RATE (1/min)	$Na_2S_2O_3$ TITRATED (ml)	GAS FEED ACCUMULATED IN WET TEST METER (liter)	DENSITY OF * OZONE-OXYGEN MIXTURE AT 70°F,6 psig (mg/1)	CONCEN-TRATION OF OZONE (mg/1)	WEIGHT % OF OZONE IN OZONE-OXYGEN MIXTURE (%)
1	0.4	21.2	1.4736	995	34.55	3.47
2	0.5	30.55	2.237	995	32.77	3.29
3	0.6	35.78	2.577	995	33.320	3.34

* Data from Welsbach Corporation

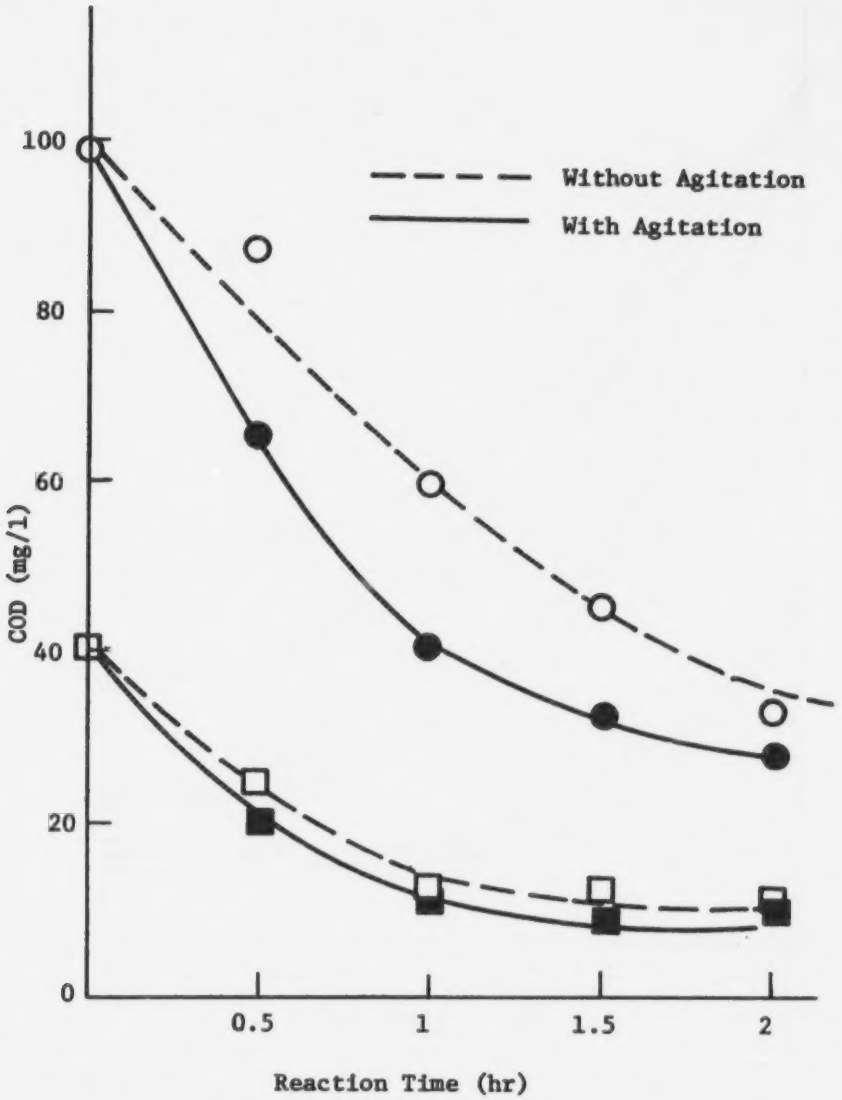


Figure 14: COD Reduction by Catalytic Ozonation: Effect of Agitation

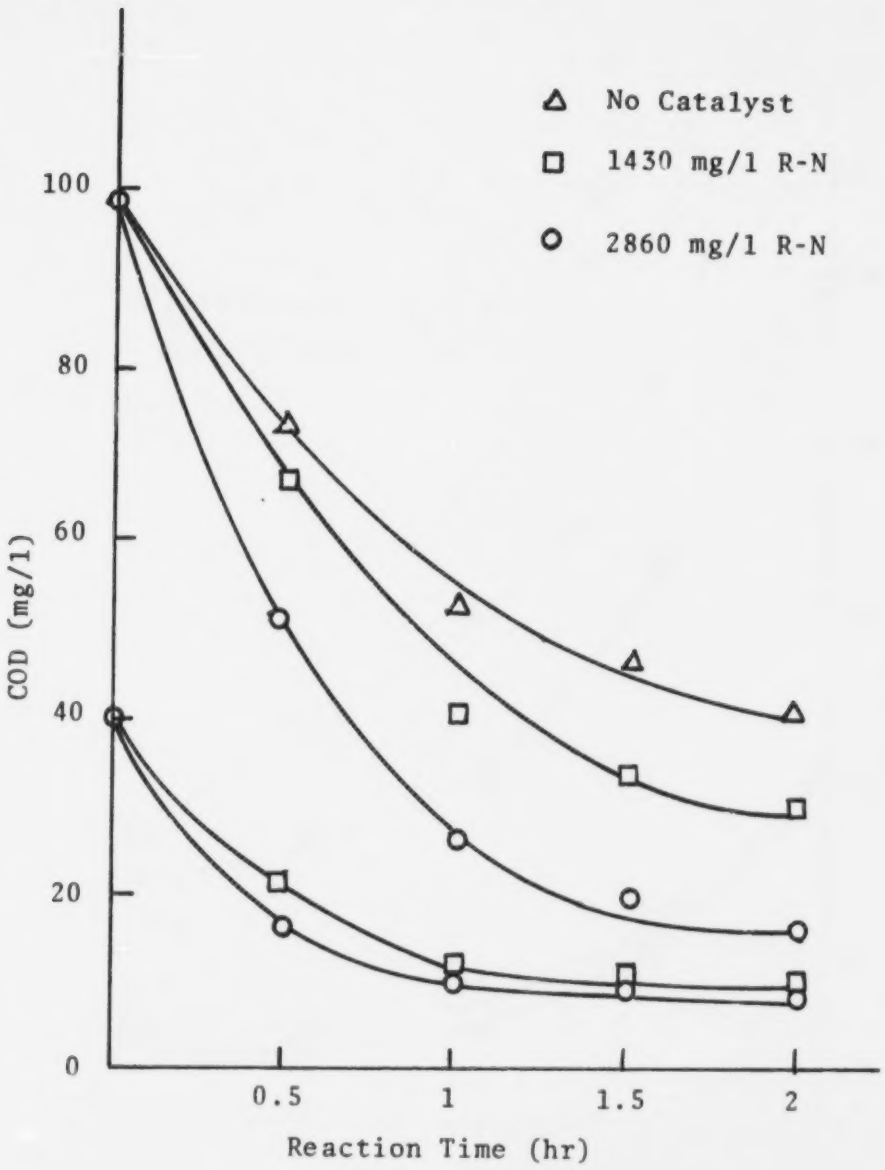


Figure 15: COD Reduction by Catalytic Ozonation: Effect of Catalyst Dose

TABLE 6: Ozone Utilization During Ozonation of Wastewater

SAMPLE	OZONE CONCENTRATION IN GAS FEED (mg/1)	OZONE CONCENTRATION IN GAS OUTLET (mg/1)	OZONE CONSUMPTION (mg/1)	WEIGHT PERCENT OF OZONE CONSUMED (%)
Ozonation w/o Agitation	32.77	25.30	7.47	22.8
Ozonation With Agitation	32.77	20.927	11.843	36.2
Catalytic Ozonation With Agitation	32.77	17.049	15.721	48

Toward the end of the period of this project, some experiments were conducted to determine if simple oxygenation or complete conversion to carbon dioxide, as measured by changes in TOC, resulted from catalytic ozonation. Using a wastewater having an initial TOC of 50 mg/l, 45% of the TOC was removed in 2 hours at a catalyst dose of 143 mg/l, and 60% of the TOC was removed at a catalyst dose of 14300 mg/l (Figure 16).

4. Conclusions of Waste Water Experiments

Summarizing all the experimental results in wastewaters, the following conclusions can be drawn:

(a) Ultrasound alone has a significant effect on the oxidation of wastewater when air is used as the feed gas. Sonocatalysis exhibits a synergistic effect; i.e., the results of sonocatalytic oxidation are better than the combined effects of sono-oxidation and catalytic oxidation.

(b) Activated Raney-Nickel was found to be a good catalyst for sonocatalytic oxidation (ultrasound, activated Raney-Nickel and air). A reduction in COD of 78% and ODI of 96% was obtained in two hours of treatment. Furthermore, this catalyst is stable under ultrasonic irradiation.

(c) At low catalyst concentration and low ozone doses, there is only a slight synergetic effect in sonocatalytic ozonation (ultrasound, activated Raney-Nickel and ozone). Sonocatalytic ozonation, however, can remove COD and ODI in wastewater.

(d) The unique combination of activated Raney-Nickel and ozone/oxygen mixtures could be a potentially effective treatment process for wastewater. Depending on the initial COD of the waste, and the concentration of catalyst, a 40% to 85% reduction in COD and a 60% reduction in TOC have been achieved for wastewater.

(e) Bacteriological examination indicates that the water samples after different treatments are free of coliform organisms.

B. Phenol Experiments

1. Different Types of Treatment

We have reported previously (3) that addition of a catalyst in the sono-oxidation of aqueous phenol retards the reaction rate. These results are reproduced in Figure 17. The reason for this inhibition was attributed to the fact that

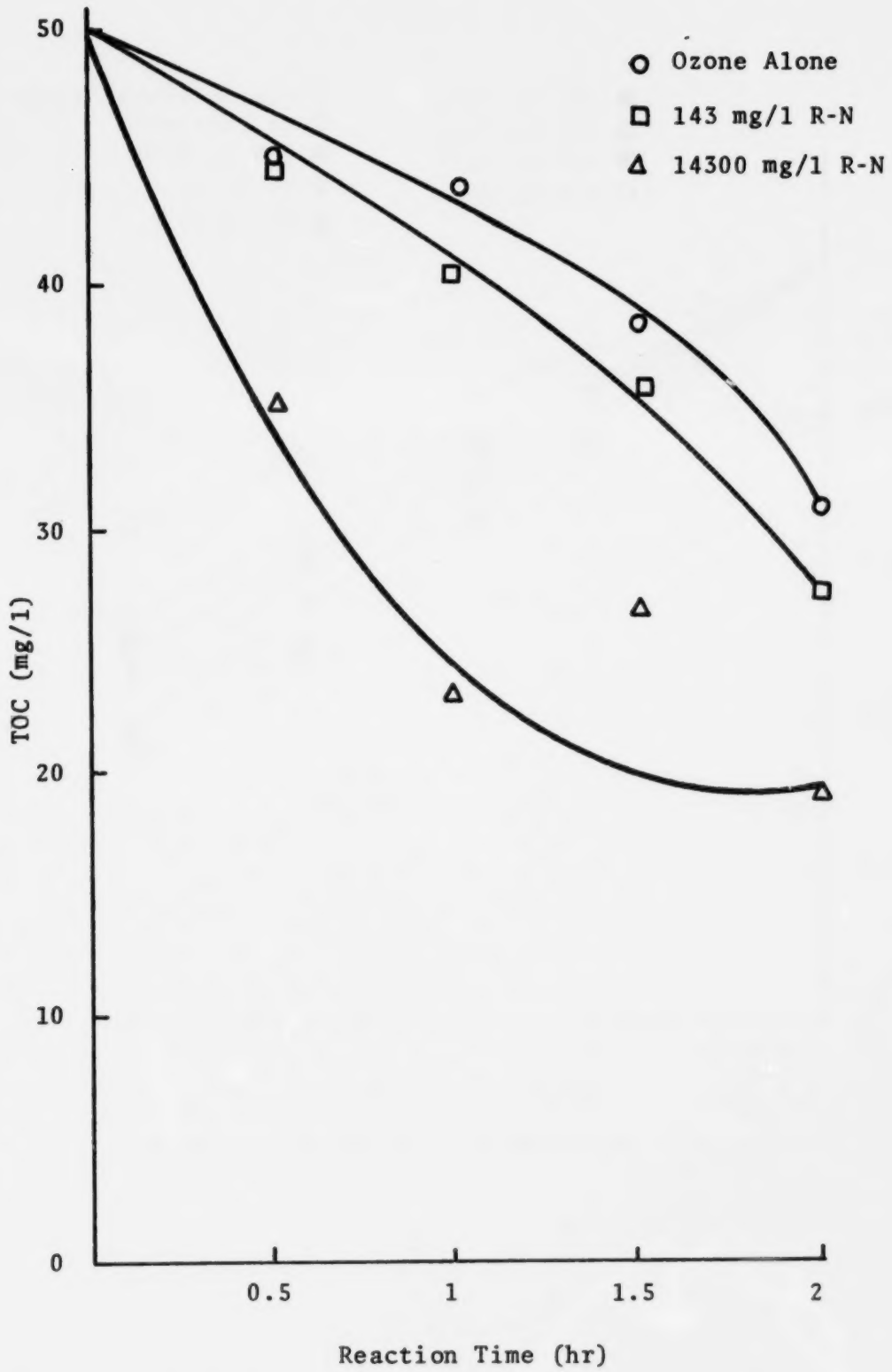


Figure 16: TOC Removal by Catalytic Ozonation

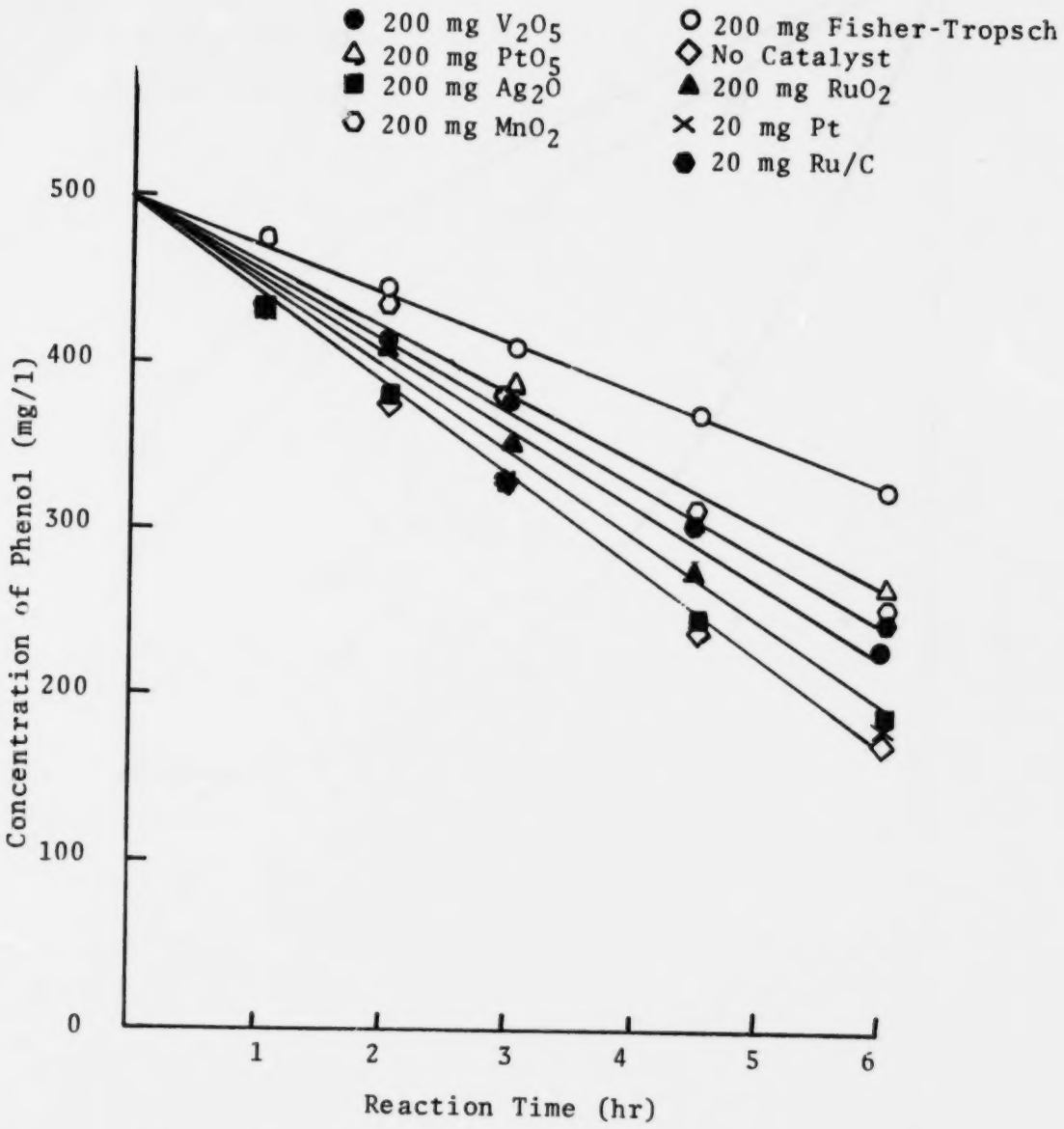


Figure 17: Sonocatalytic Oxidation of Phenol

there is no catalytic oxidation of phenol at room temperature. In certain situations, therefore, solid catalysts in the solution actually interfere with ultrasonic waves transmitted from the generator and reduce the effect of ultrasonic irradiation.

Figure 18 shows the experimental data of various types of treatment for phenol solutions. In all the experiments, 200 ml of 0.00532M aqueous phenol solution (500 mg per liter) were used. Analyses were performed mainly by gas chromatography. Treatment time was three hours and samples were withdrawn every half hour. The results are summarized in the following:

(a) The phenol solution was dosed with 160 mg of activated Raney-Nickel and stirred with a magnetic stirrer. No change in the phenol concentration was observed.

(b) About 65 mg ozone per hour (1.15 mg per liter) were bubbled through the phenol solution. The treatment caused a 31% decrease in phenol concentration in three hours.

(c) The phenol solution was irradiated by ultrasound. An almost linear decrease of the phenol concentration of 60% occurred in three hours.

(d) A combined treatment of ultrasonic irradiation and ozone bubbling showed a decrease in phenol of 91%.

(e) 160 mg of activated Raney-Nickel in the phenol solution irradiated with ultrasound causes no appreciable change in comparison with the ultrasonic irradiation alone (60% decrease).

(f) 160 mg of activated Raney-Nickel together with ozone bubbling effects the phenol decrease considerably, 68% compared with 31% ozone bubbling alone.

(g) The lowest phenol concentration after three hours' treatment was reached by a combination of ultrasonic irradiation, ozone bubbling and 160 mg of activated Raney-Nickel. The decrease was 95%.

From the experimental data, two important points are revealed. First, it verifies the previous results that catalyst actually inhibits the sono-oxidation. However, catalysts promote the sono-ozonation process because the ozonation of phenol is promoted by catalysts. Secondly, catalytic ozonation alone effectively oxidizes phenol without insonation.

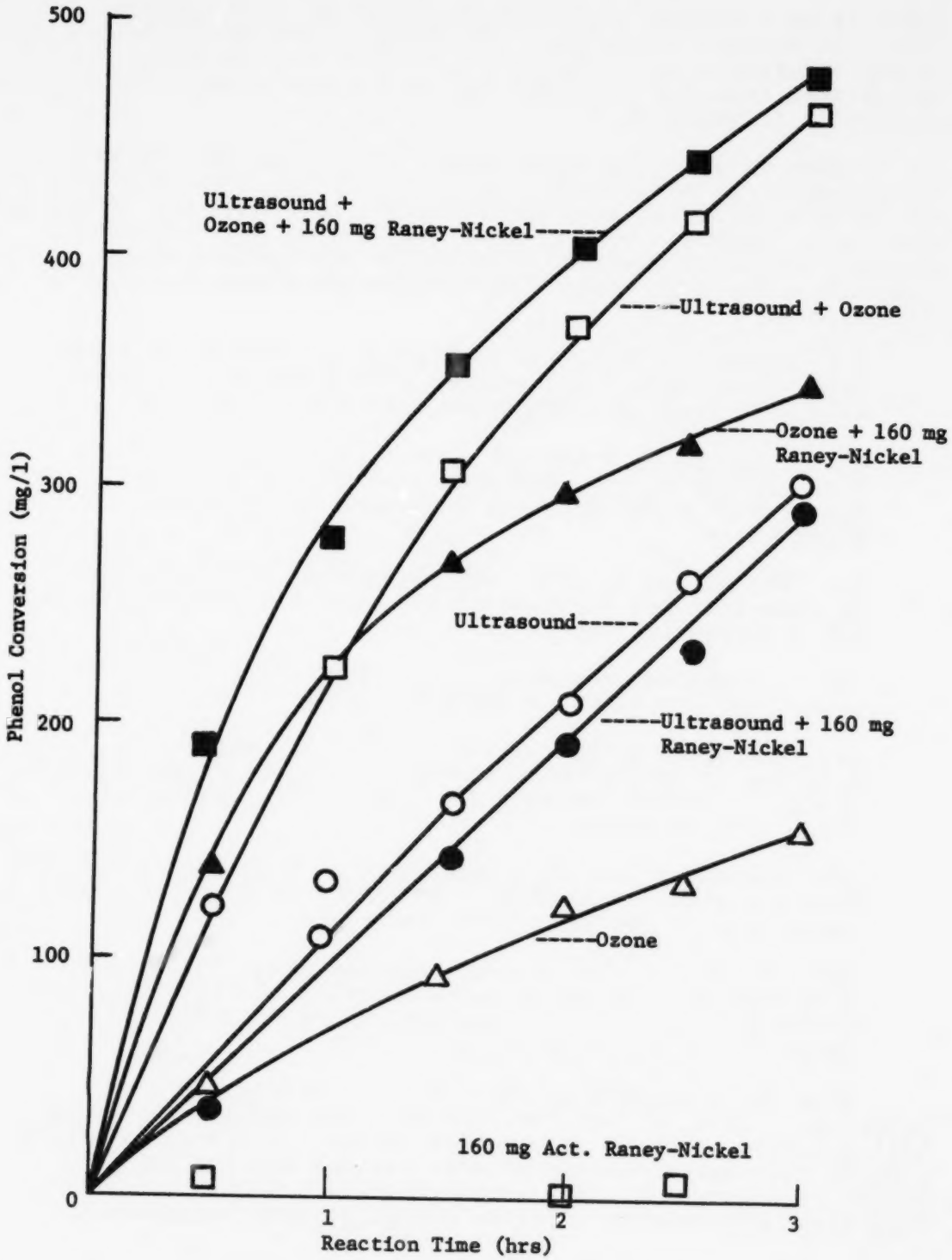


Figure 18: Phenol Conversion by Different Oxidative Treatments

2. Variation of the Amount of Catalyst

A set of experiments were conducted to study the effect of the variation of the amount of activated Raney-Nickel in the different types of treatment. The results are summarized as follows:

(a) Different amounts of activated Raney-Nickel in aqueous phenol solutions were agitated with a magnetic stirrer; no conversion of phenol was observed in any case.

(b) Aqueous phenol containing different amounts of activated Raney-Nickel under ultrasonic irradiation did not show significant differences in comparison with the results without a catalyst.

(c) An increase in the amount of catalyst during ozonation, however, causes an increase in the amount of phenol converted. The results are shown in Figures 19 and 20.

(d) These phenomena of maximum catalyst dose for catalytic sono-oxidation and optimum catalyst dose for sonocatalytic ozonation are clearly observed in Figure 20. Increasing the amount of catalyst during sono-ozonation increases phenol conversion to a maximum, but further increases in a catalyst decrease phenol conversion because of interference with insonation. (Figure 20)

In all cases, sonocatalytic ozonation is better than either catalytic ozonation or sonocatalytic oxidation. As is seen, when the amount of catalyst in the aqueous solution exceeds the optimum level, a decrease in rate of conversion results.

3. Ozone Consumption

For both process application and mechanistic study, it was of interest to evalute how much ozone is consumed in different types of treatment. A set of experiments were performed in which ozone concentrations at the inlet and outlet of the reaction system were determined by iodometric methods at different times. The experimental results for a two-hour reaction period are shown in Table 7. As expected from prior results, the use of insonation and catalyst resulted in the greatest utilization of ozone. Parallel conclusions on phenol conversions and ozone consumption can be drawn for both the sono-ozonation and catalytic ozone processes. In comparing ozone utilization by aqueous phenol solution to utilization by distilled water under similar experimental conditions, it appears that a significant amount of ozone is used in the oxidation of phenol. Furthermore, both ultrasound and catalyst have the

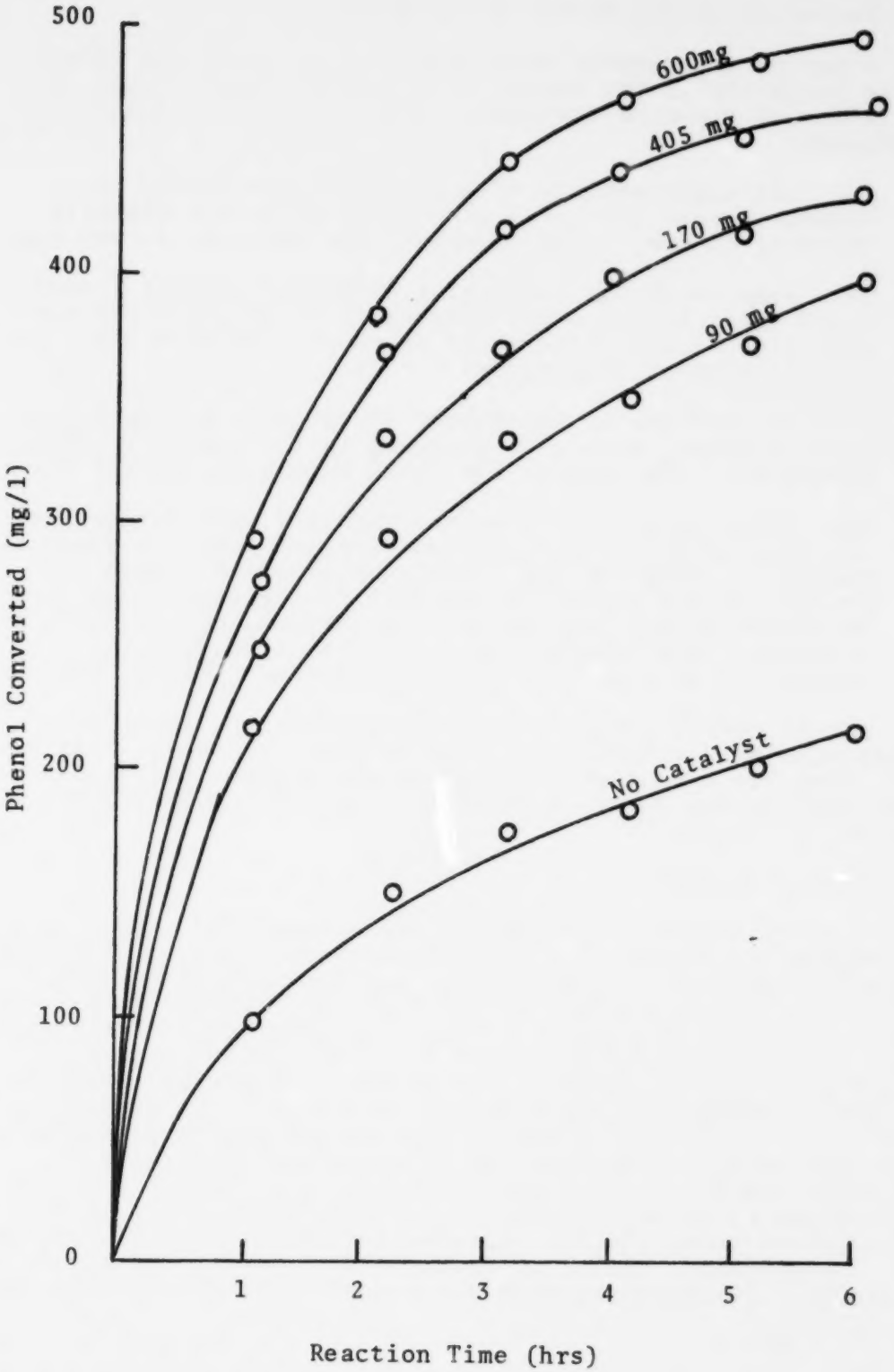


Figure 19: Catalytic Ozonation of Phenol: Effect of Catalyst Dose

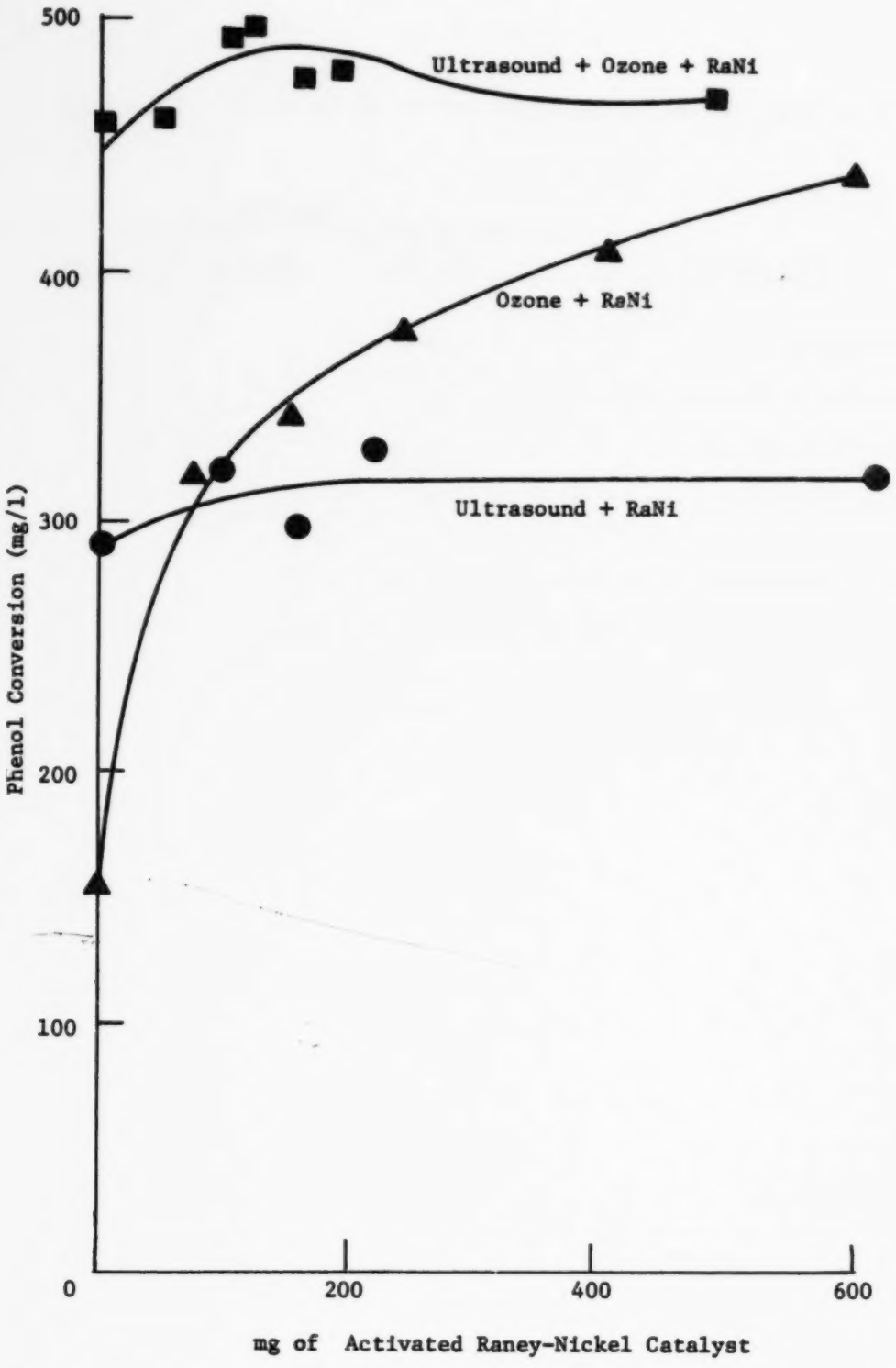


Figure 20: Comparison of Phenol Conversion with Variation of the Amount of Catalyst (Three Hours Treatment)

TABLE 7

Milligrams Ozone Decomposed and Used in 2-Hour Reaction

Treatment	SAMPLE	
	Distilled Water	200 mg/l Phenol Solution
Ozonation	8	41
Catalytic Ozonation	10	76
Sono-ozonation	13	96
Sonocatalytic Ozonation	23	120

Ozone produced in 2 hours: 145 mg

Catalyst: 200 mg activated Raney-Nickel/200 ml

ability to either absorb or decompose ozone according to the experimental data of distilled water. Therefore, residual ozone in the solutions is small.

4. Analysis of Chemical Oxygen Demand

In the previous experiments, analyses of phenol were performed by gas chromatography, which shows only the decrease in the phenol concentration. Since it is desirable to get information about the oxidation state of the compounds formed, a Technicon AutoAnalyzer was used to determine Chemical Oxygen Demand (COD). For this reason, another set of experiments was performed starting with a 40 ppm phenol solution and treating it for seven hours by different oxidation processes. The following treatments were compared to each other: ozonation versus catalytic ozonation; sono-oxidation versus sonocatalytic oxidation; and sono-ozonation versus sonocatalytic ozonation. The results are shown in Figures 21, 22 and 23 respectively. In every case, the average oxidation state of the reaction mixture gets higher with increasing time of treatment. This is represented by a decrease in the chemical oxygen demand (COD). However, whereas phenol is no longer detected after 2 1/2 hours, the COD values decrease rather slowly. Apparently, the rate of phenol conversion to catechol and resorcinol is greater than the rates of subsequent steps leading to higher oxidation states. Nevertheless, in the case of sonocatalytic ozonation, the decrease in COD to 12% after seven hours of treatment is considerable, while catalytic ozonation alone reduces COD to 35%.

In Figure 24, the COD removed is plotted against time for different types of treatment of aqueous phenol solutions at 500 ppm. Sonocatalytic ozonation (ultrasound, activated Raney-Nickel and ozone) is the best combination for removing COD. Both catalytic ozonation and sono-ozonation are superior to ozonation alone.

A Beckman Model 915 Total Carbon Analyzer was used to determine whether the carbon contents of the aqueous phenol solution has been changed during treatment by ozonation and catalytic ozonation. Data indicated that the TOC was reduced very slowly. This would indicate that while most of the phenol in solution is converted into compounds of higher oxidation states, only a small part is converted to carbon dioxide during treatment. These results are shown in Figure 25 and should be compared to Figure 24.

5. Determination of the Reaction Products

a. Analysis by UV - Spectrophotometry

Since the gas chromatograph method was used primarily for phenol determinations and since the method does not supply information about the reaction products (beside the phenol peak, no other peaks were observed),

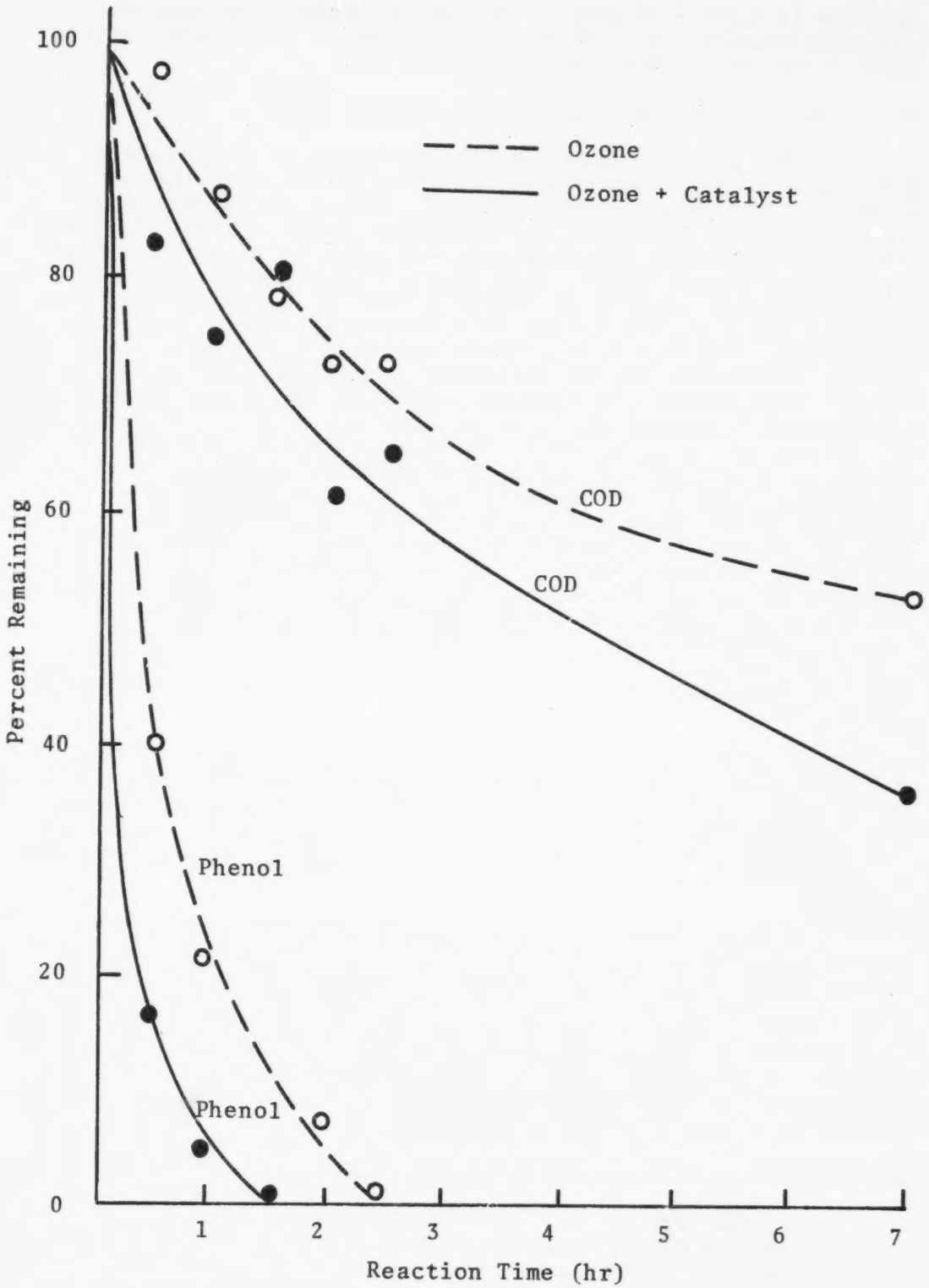


Figure 21: Conversion of Phenol and COD Removal by Ozonation: Effect of Catalysis by Activated Raney-Nickel

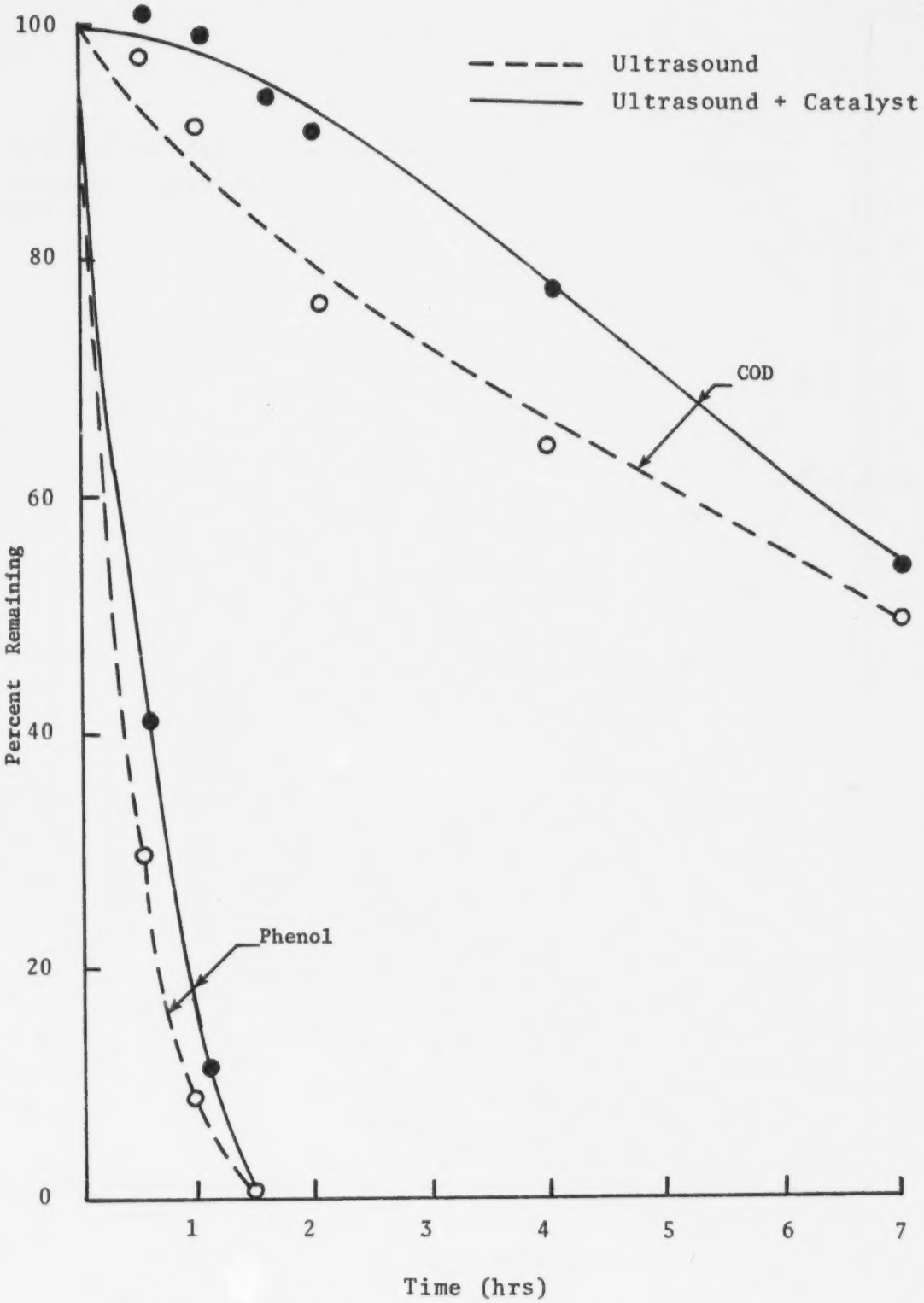


Figure 22: Conversion of Phenol and COD Removal by Sono-Oxidation: Effect of Catalysis by Activated Raney-Nickel

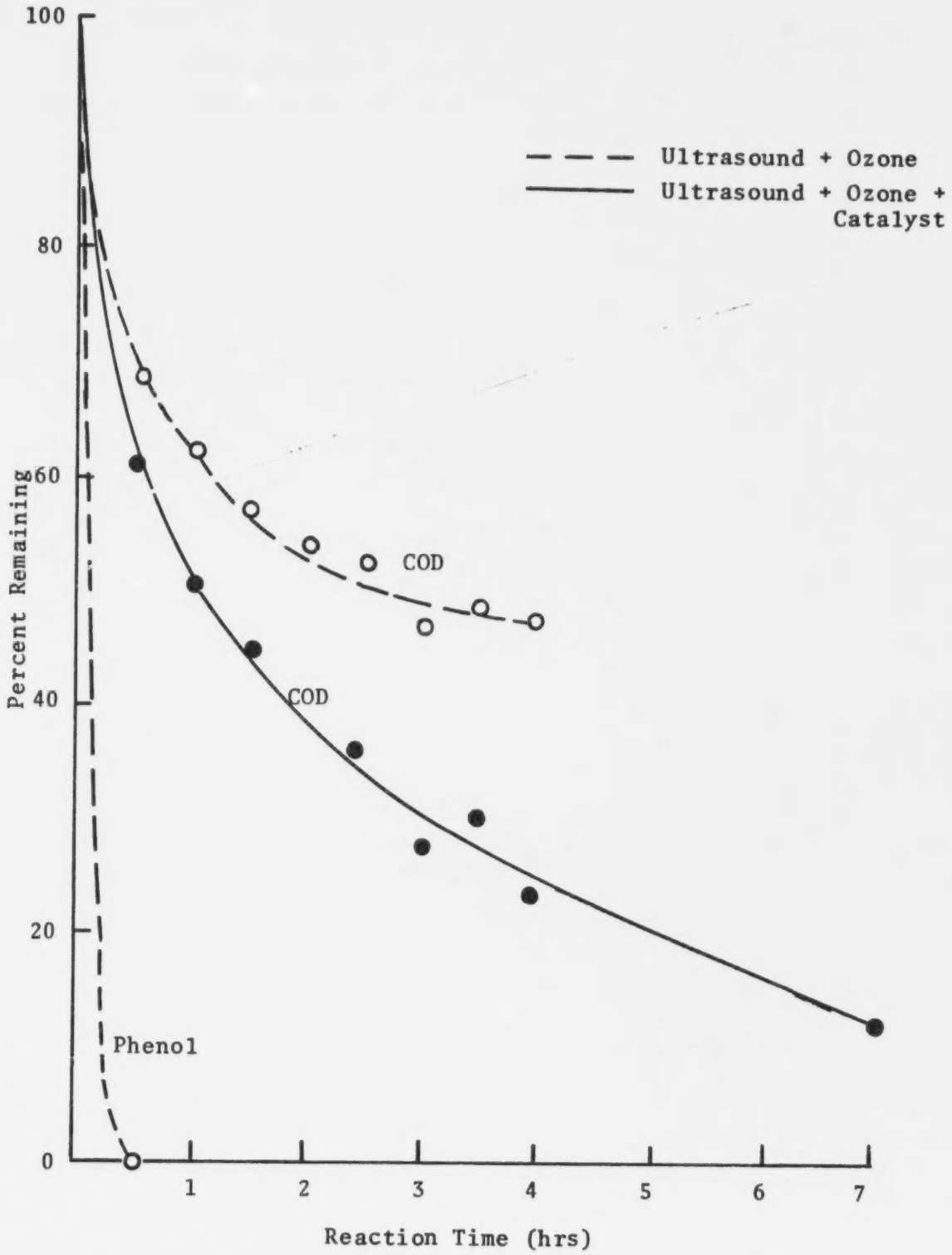


Figure 23: Conversion of Phenol and COD Removal by Sono-ozonation: Effect of Catalysis by Activated Raney-Nickel

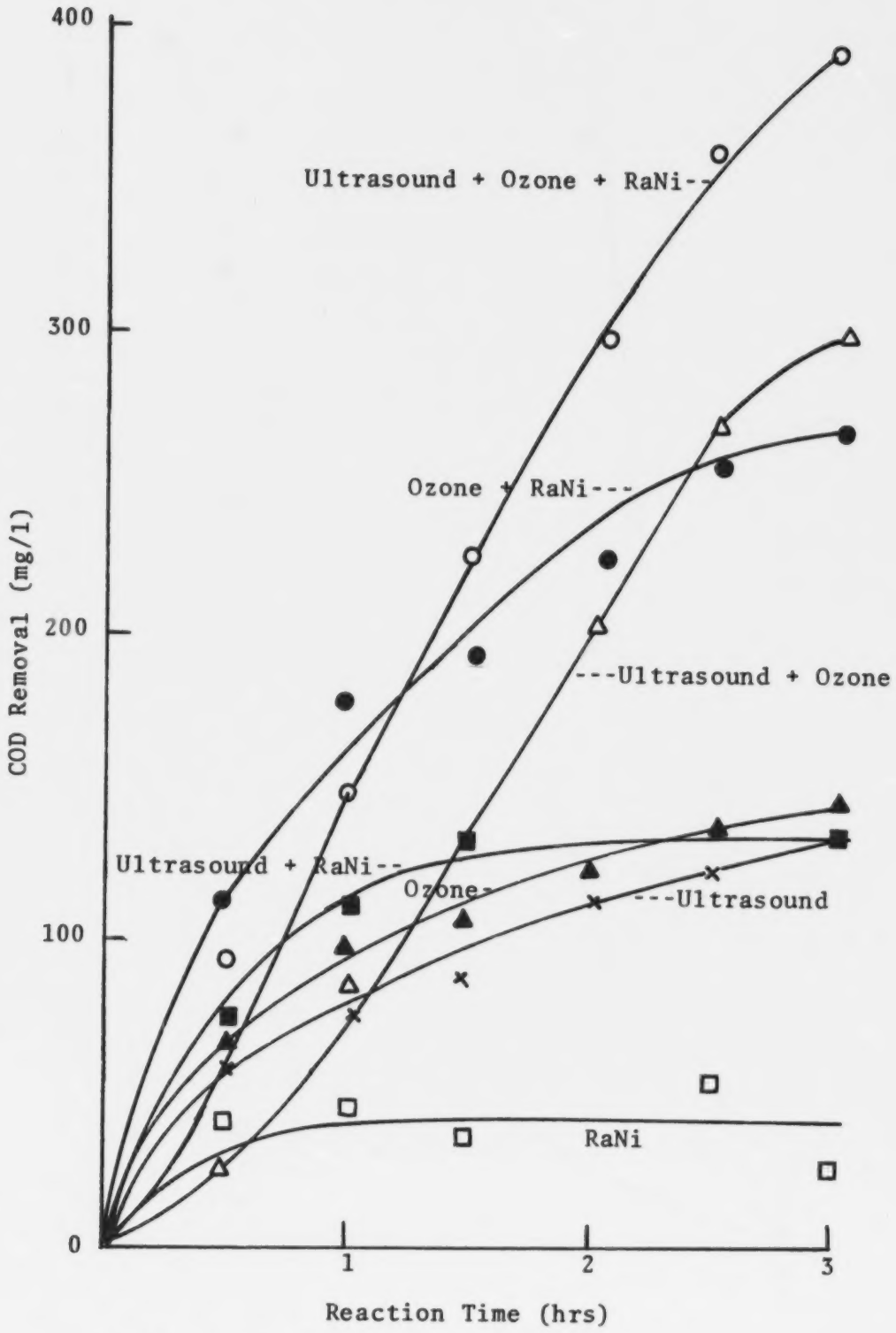


Figure 24: Comparison of COD Removal from Aqueous Phenol Solutions by Different Types of Treatment

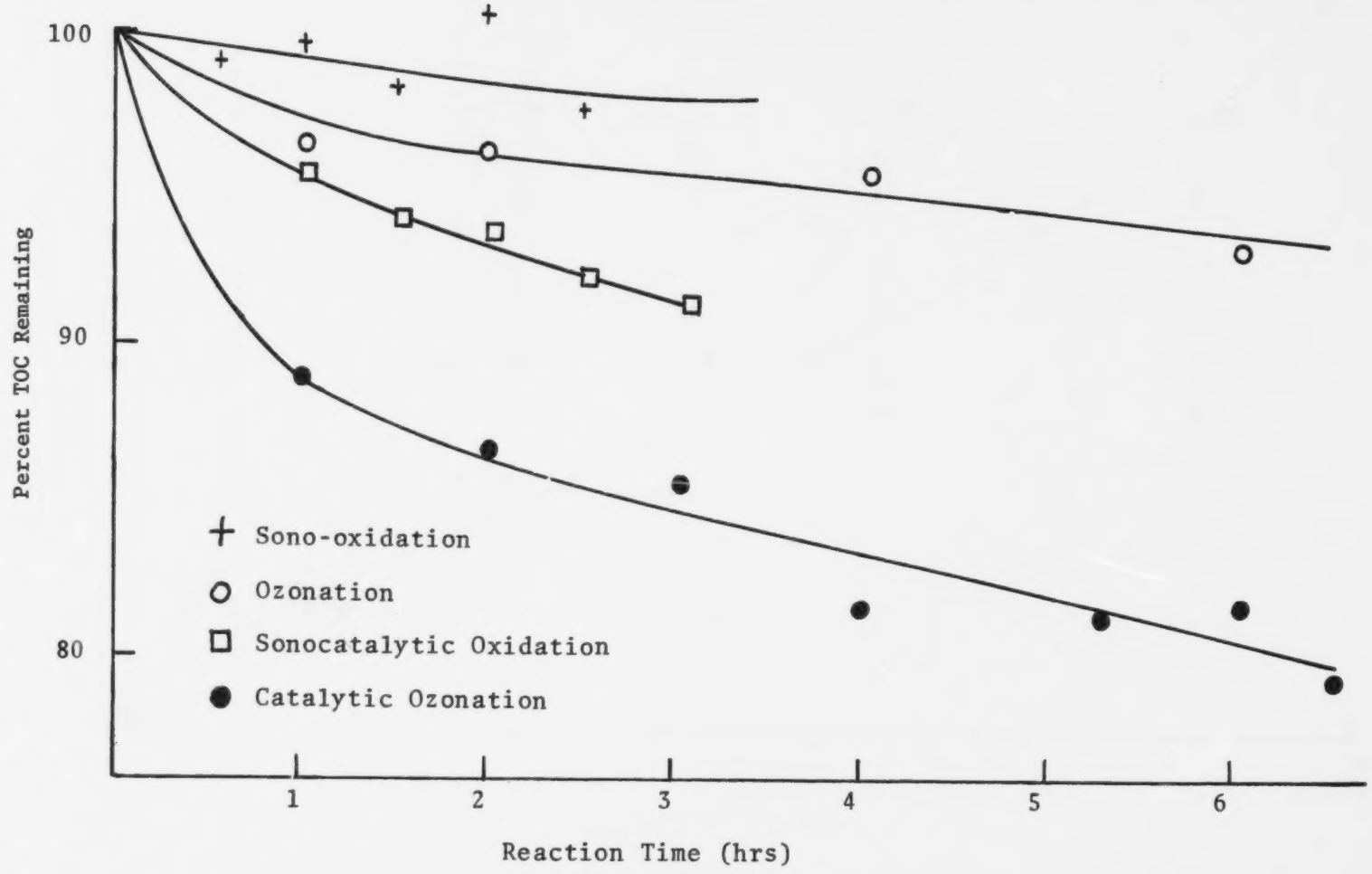


Figure 25: TOC Removal in Aqueous Phenol Solution

an ultraviolet-spectrophotometer was used to analyze samples. Phenol in water exhibits an absorption band at about 270 mm. This band corresponds to the weak 260 mm band of benzene, which is the forbidden transition to a homopolar excited state. The substituted auxochrome OH, which is a polar group containing unshared electrons, shifts the band to longer wavelengths and also intensifies it. Figure 26 shows UV spectra obtained after different times of sono-ozonation. It is seen that the vibrational structure of the 270 mm band disappears. This is generally the case when the substituent is a polar group, and a polar solvent like water is used. However, the increasing background in the UV spectra makes a quantitative analysis almost impossible. On the other hand, this background points to the formation of one or more new compounds. In Figure 27, the spectra of treated solutions are compared to that of the starting material, and new absorption bands at about 280 and 230 mm can be seen. Figure 28 shows that a mixture of hydroquinone and catechol in aqueous phenol solution furnishes a similar spectrum. It is assumed, therefore, that both hydroquinone and catechol are formed. Figure 29 shows the spectra of reaction products after six hours of different treatments. Considering spectrum "d" in this plot, it seems that the intermediates, catechol, resorcinol and others, have disappeared under the more powerful treatment (sonocatalytic ozonation). This observation is in agreement with the observation that initially, the solution becomes yellow but after a longer time, it becomes colorless again. In contrast, some hydroquinone and catechol are left in the solution under either ozonation or catalytic ozonation.

b. Analysis by Thin Layer Chromatography (TLC)
Thin layer chromatography was used to acquire more information about the reaction products (see C. orthochloronitrobenzene for description of the Techniques). The time of treatment was varied in a set of experiments with a 500 mg/l aqueous phenol solution (100 mg phenol in 200 ml H_2O) treated by ultrasound, ozone, and activated Raney-Nickel. After a given reaction time, the reaction mixtures were extracted with ether, most of the ether was vaporized, and the concentrated extracts were put on a thin layer plate. Subsequent to ether extraction, the reaction mixtures were freezedried and the residues were dissolved in acetone, The acetone solutions were concentrated and put on a thin layer plate (chromatograph e). The distribution of ether extractable compounds on the TLC plate is shown in Figure 30. After one hour of sonocatalytic ozonation, an additional less polar product can be observed at the top

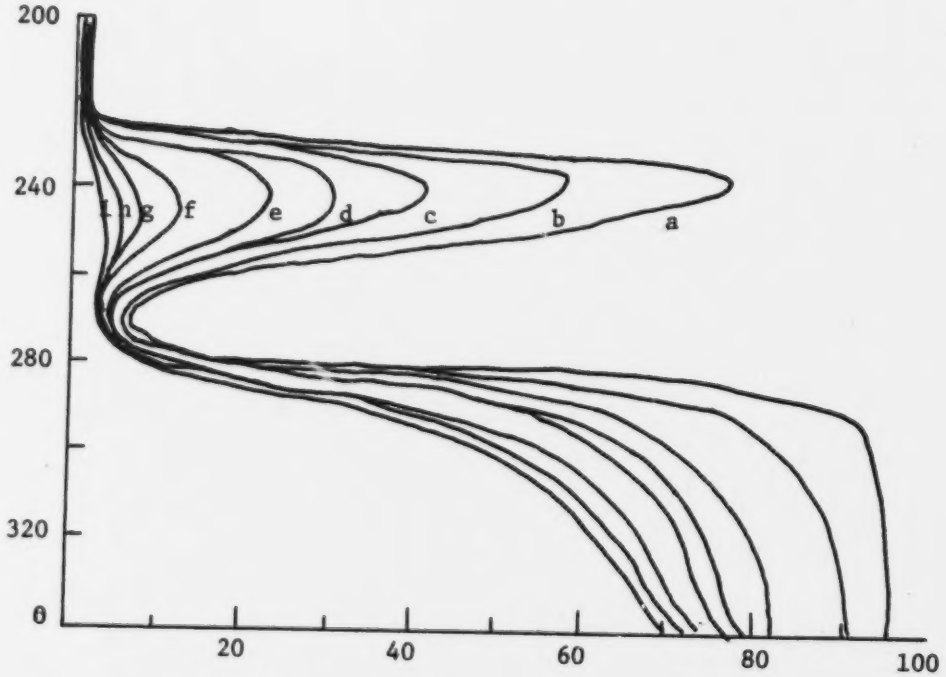


Figure 26: UV Spectra, Sono-ozonation of Phenol Solution

a: starting material; b: after 1/4 hr; c: 1/2 hr; d: 3/4 hr; e: 1 hr; f: 1 1/2 hr; g: 2 hrs; h: 2 1/2 hrs; i: 3 1/2 hrs treatment.

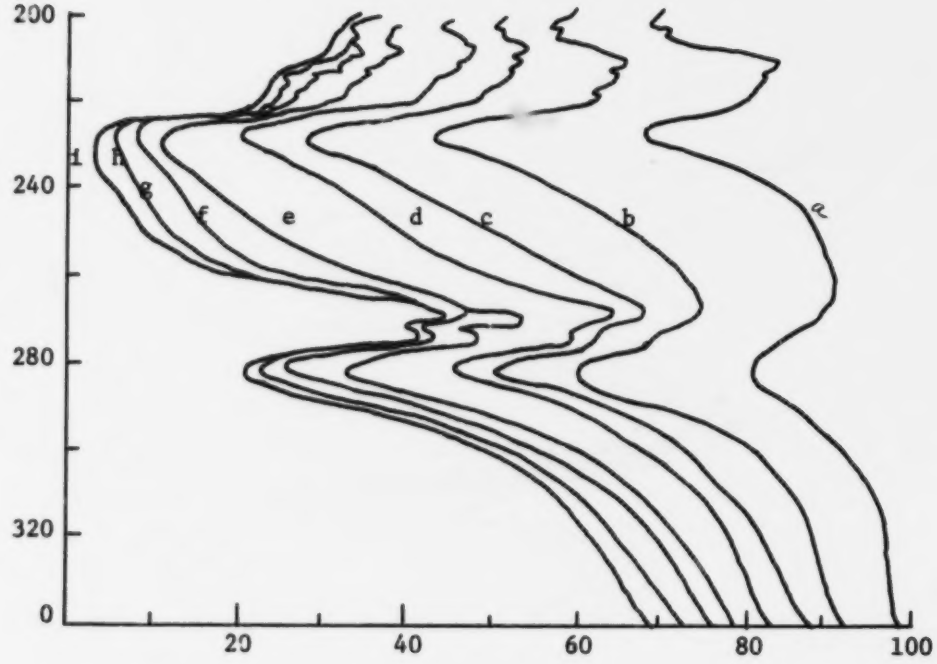


Figure 27: UV Spectra, Sono-ozonation of Phenol Solution

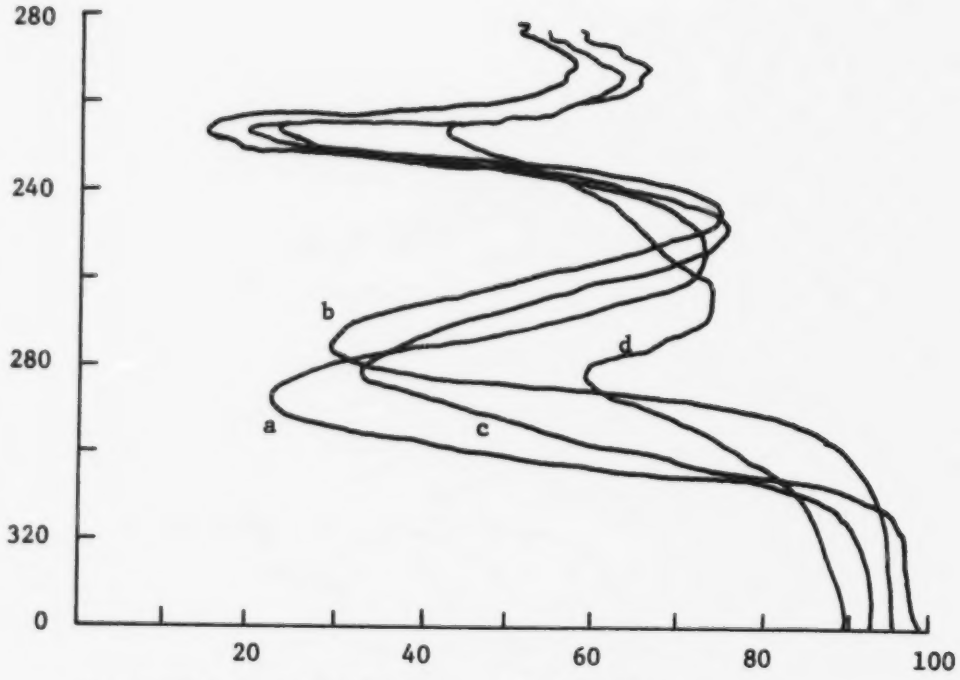


Figure 28: UV Spectra of Synthetic Mixture and Reaction Products

a: Hydroquinone, b: Catechol, c: Hydroquinone and Catechol, d: Aqueous Phenol solution after 1/2 hour treatment with U.S. + O_3

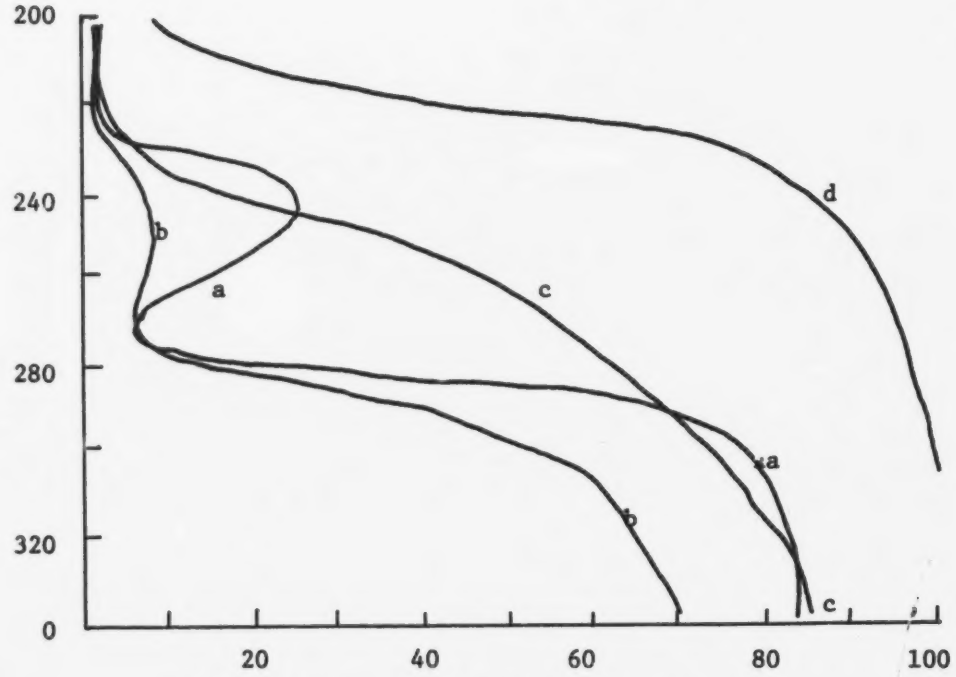


Figure 29: UV Spectra of Reaction Products for Different Types of Treatment of Aqueous Phenol Solution

a: O_3, b: O_3 + 0.5 gr Ni, c: O_3 + U.S., d: O_3, U.S., and 0.5 gr Ni using a more powerful U.S. generator)

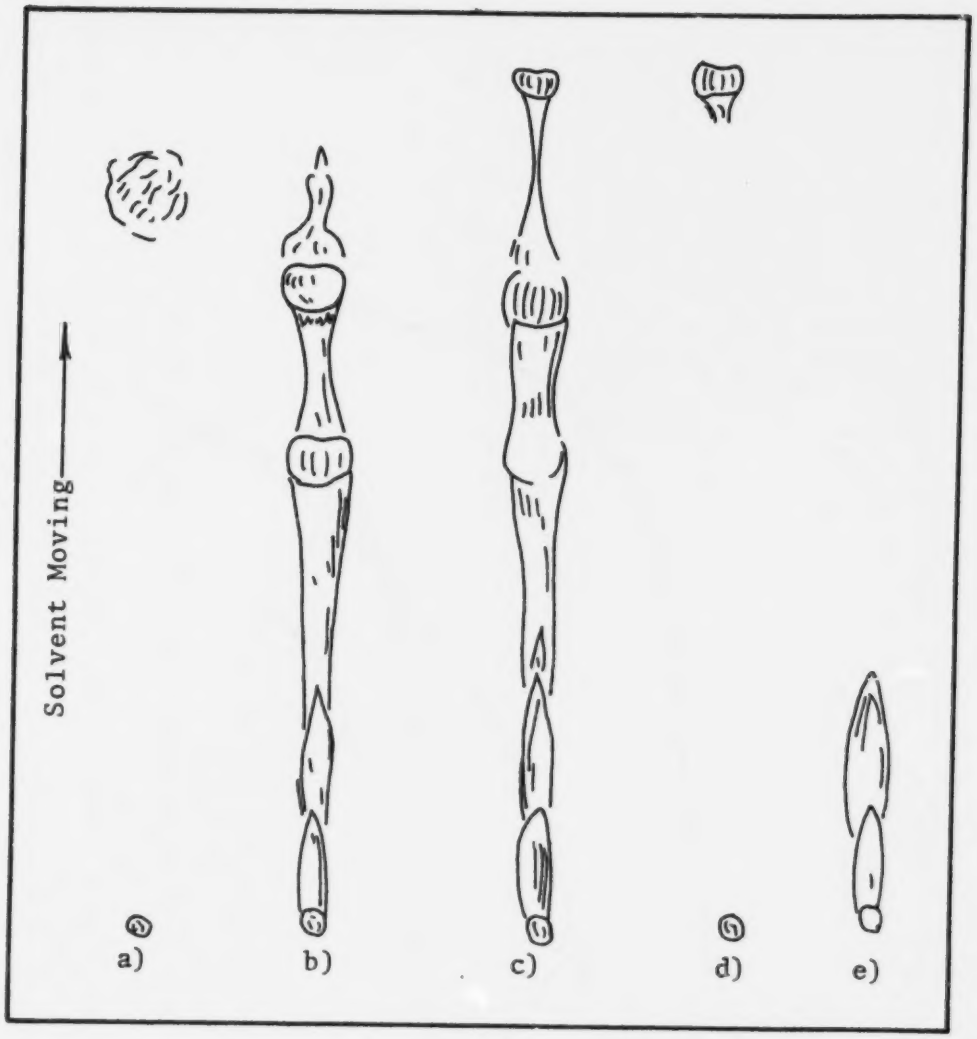


Figure 30: Thin Layer Chromatograms

(a): starting material; b)c)d): concentrated ether extract of solutions treated for b) 1 hour, c) 3 hours, d) 5 hours; e) solid residue dissolved in acetone.

of the thin layer plate (chromatogram c). This compound is the only one which remains after a treatment of five hours (chromatogram d). Only the lower part of the chromatograph b remains.

In order to get enough material for infrared and mass spectrometric analyses, sonocatalytic ozonations of aqueous phenol solutions of higher concentrations (1 g or 3 g phenol in 200 ml H_2O) were conducted for longer periods (16 hours, 20 hours).

The compounds formed in several runs were combined, and extracted with ether. The ether extract was concentrated and thrice separated by preparative TLC. These relatively pure materials were analyzed by mass spectrometry. In the spectra of the less polar compounds, the masses 108 (quinone) and 110 (hydroxybenzenes) appear, as well as mass 127 (protonized pyrogallol). The most polar compound, which remains at the starting point on the TLC plate, shows a main peak at m/e = 98 in its mass spectrum. This could be the molecular peak of 2-cyclohexene-1-ol or cyclohexanone. However, this would mean that a reduction of phenol occurs in the reaction. Although reduction of orthochloronitrobenzene occurs (see Section C), it seems rather unlikely here. While all spectra contained several impurities, along with small amounts of solvent used for separation on TLC, the spectra show positive evidence of the presence of compounds like catechol, hydroquinone, and resourcinol, as well as quinone and pyrogallol, in the reaction mixture.

After ether extraction, the remaining aqueous solution was freezedried and the solid residue treated with diazomethane. If the residue is an acid, the corresponding methyl ester should be formed. IR and NMR spectra of the reaction product show evidence of esters, although it was not possible to evaluate the spectra quantitatively.

6. Conclusions of Phenol Experiments

a. Phenol in aqueous solution does not react with oxygen (air) under the influence of catalysts. On the other hand, phenol is oxidized by air and ultrasonic irradiation. However, catalysts interfere with sono-oxidation.

b. Phenol reacts with ozone slowly, but activated Raney-Nickel catalyzes the reaction. Application of activated Raney-Nickel, ozone, and ultrasound gives the best performance under the same operating conditions.

c. By measuring changes in phenol concentration, COD, and the TOC of the reaction mixtures, it was found that the rate of phenol disappearance is much faster than the rate of TOC removal. Apparently, phenol is converted sequentially to more and more highly oxidized compounds,

while only a small portion is actually converted to CO_2.

d. Intermediate products in the reaction mixture are identified as catechol, hydroquinone, quinone and pyrogallol; compounds which are more highly oxidized than phenol. However, these compounds also disappear during sono-catalytic ozonation showing that even more highly oxidized compounds are formed.

e. Both catalytic, and sonocatalytic, ozonation would apply as treatment processes for phenol wastes.

C. Orthochloronitrobenzene (OCNB) Experiments

1. Reaction Mixtures

Reaction mixtures consisted of 200 ml distilled water, 5 grams of freshly sublimed OCNB, and 5 grams of aluminum powder or 2 grams of activated Raney-Nickel catalyst. The gas was oxygen, air, or ozone/oxygen mixtures. Since much more OCNB was present than was required for saturation, solid substrate was present in the reaction mixture and tended to sublime and become entrained in the gases. The amount collected in the trap depended on the duration of sparging, the flow rate of gases, and the initial concentration of OCNB. For example, after six hours insonation and air sparging, 0.30 grams of OCNB was recovered in the cold trap. This does not occur, however, if only a saturated solution (approx. 2×10^{-3}M) of substrate is used.

Some experiments were run with a saturated solution of OCNB in water. To 200 ml of this solution was added 2 grams of either aluminum powder or activated Raney-Nickel. The sample was irradiated with ultrasound at 800 KHz and sparged with an ozone/oxygen mixture for 24 hours. At the end of the reaction time, neither OCNB, nor any products, could be detected by thin layer chromatography in the reaction mixture. Since the starting material is easily detected in an identical experiment in the absence of catalyst, it must be concluded that the sonocatalytic reactions ultimately destroy OCNB.

2. Isolation and Identification of Products

After insonation for 6 hours, the reaction mixture is filtered to remove catalyst and solid OCNB. The yellow aqueous solution of intermediates, products, and unreacted OCNB, is separated by ether extraction into two fractions. Several products can be seen upon thin layer chromatographic analysis of reaction mixtures. The ether extract, after concentration and TLC analysis (silica gel and 60/40 cyclohexane/ethyl acetate solvent) separates into three major

components (A, B, and C) plus OCNB. The aqueous portion, upon being concentrated by freeze drying, consists of a dark brown tacky material. It is highly polar; not being eluted from a TLC plate under the conditions given above. A test for aluminum is faintly positive when the aqueous portion (about 200 ml) is concentrated to 0.5 ml; however, no positive test is obtained with the unconcentrated reaction mixture. Qualitatively, it appears that bubbling ozone/oxygen through the reaction mixture slightly increases the reaction rate. On the other hand, when nitrogen is the sparging gas, the same types of products are obtained, but more slowly. While the isolations were made from the aluminum-catalyzed reactions, active Raney-Nickel, compared to aluminum, appears to give lower yields and slightly different products.

Although no products are found in the absence of ultrasound at room temperature in 48 hours, reaction does occur in boiling water. After 100 hours of refluxing OCNB, water, aluminum powder and air and then isolating the organic materials, a TLC separation is obtained which is similar to the separation obtained from the sonocatalytic reaction mixture. The major difference is that compound A is the main product, and little of the dark brown, tacky, material is formed. In the refluxing experiment, copious quantities of $Al(OH)_3$ are formed, which is in contrast to insonation at room temperature. Under similar reflux conditions, activated Raney-Nickel also produces products; however, some new products are formed.

By repeating sonocatalysis of OCNB several times, and combining the reaction mixtures, it was possible to amass sufficient material to isolate each of the three major components; A, B, and C. Actually, the dark brown, tacky, material was the major product but was not resolvable by our procedures.

3. Isolation and Identification of Compound B

Compound B was separated from the combined ether extracts from ten runs (5 gms OCNB, 5 gms Al°, 200 ml H_2O, air, 6 hours reaction). The combined extract was eluted through a silica gel column (50 gm) with petroleum ether, then with 10% ethyl ether in petroleum ether, and finally with 20% ethyl ether in petroleum ether. In the first fraction, compound B elutes along with small amounts of other products and some OCNB, but in later fractions, only OCNB elutes. Products not eluted with the ethyl ether-petroleum ether mixtures are eluted with methanol. Repeated preparatory TLC (8" x 8" plate of mixture of Silica gel G and Silica gel HF 254 + 366 in 3/2 ratio developed with a 1/1 mixture of cyclohexane and ethyl acetate) of combined ether extracts yields a mixture of compound B

contaminated with OCNB. Final elution with a 60/40 mixture of cyclohexane/ethyl acetate separates compound B from OCNB.

Further purification of B by sublimation at 140°C and 1 mm Hg gives an orange yellow solid. Infrared analysis in Nujol shows absorption bands at 1610, 1580, 1370, 1340, 1250, 1055, 1025, and 750 cm^{-1}. The mass spectrum (10 volts) shows weak parent peaks at m/e of 270/268/266 and major fragments at 254/252/250, 233/231, 141/139, 113/111, and 38/36. An elemental analysis results in the following elemental distribution: %C: 56.00, %H: 2.99, %N: 10.79, and %Cl: 25.14. Based on these analyses, compound B is postulated to be 2,2'-dichloroazoxybenzene (Figure 31).

4. Isolation and Identification of Compound C

Since compounds A and C have similar retentions on TLC analysis, they are easily separated from B and OCNB, but not easily from each other. First, the ether extract was concentrated and most of the OCNB was removed by sublimation at 50°C and 1 mm Hg. The residue was separated by repeated preparative TLC (8" x 8" plate of silica gel B/silica gel HF 254 in 3/2 ratio developed with a 60/40 ethyl acetate/cyclohexane mixture). Combinations of several TLC separations yielded compound C which was further purified twice by sublimation at 138°C and 1 mm Hg to a yellow solid (20 mg from 10 gm starting OCNB). Infrared analysis of compound C shows major adsorption at 3290, 3380, 1500, 1270, 1200, 1040, and 910 cm^{-1}. The mass spectrum (10 volts) shows major peaks at m/e of 143/145, 141 and 44; and minor peaks at 113, 80, 78, 58 and 36/38. Elemental analysis of compound C results in the following: C: 50.51%, H: 4.32%, N: 9.07%; and by difference (because insufficient sample was sent for analysis) O: 11.24% and Cl: 24.89%. We believe Compound C is ortho-chlorophenylhydroxylamine (Figure 31).

5. Isolation and Identification of Compound A

Compound A was isolated in the same manner as C except with more difficulty because of its lower concentration. Purification by double sublimation at 140°C and 1 mm Hg yielded a dark red solid. Compound A apparently decomposes or oxidizes on standing because all the analytical data indicated that compound A was a mixture; e.g., mass spectral analysis changed with time, and elemental analysis showed C: 66.71, H: 4.40, H: 11.41, Cl: 2.85, O: 14.63. Different isolations of compound A, however, always exhibited a mass spectrum peak at m/e 212 and we believe this to be the parent peak. A possible structure is shown in Figure 31. This compound of that structure would exhibit m/e 212 and the elemental analysis would be that of a mixture which would be approximately 90% compound A and 10% compound C.

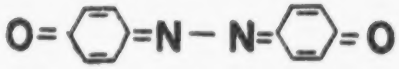
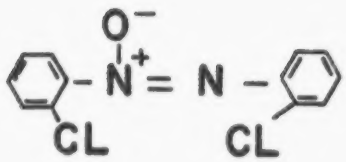
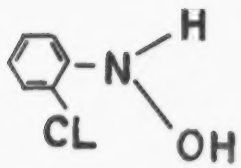
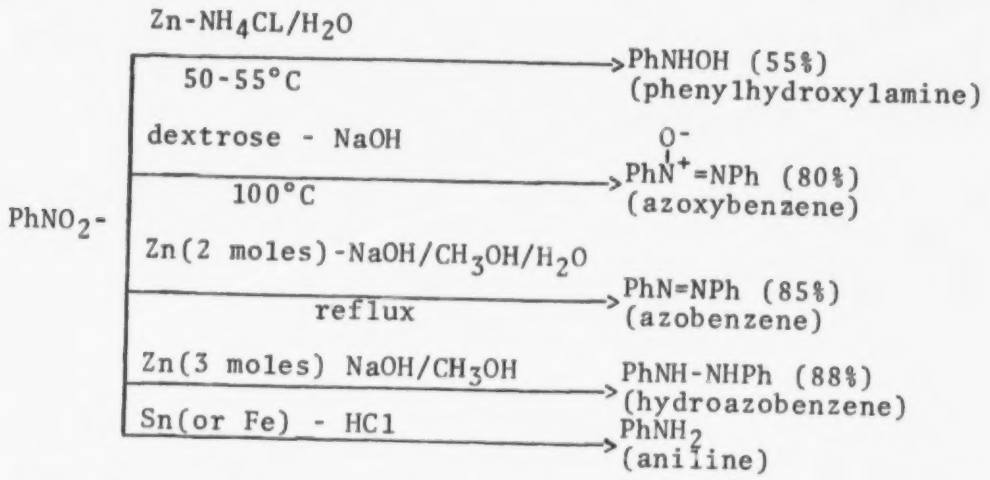
Compound		Structure
A (suggested)		
B	2,2'-dichloroazoxy-benzene	
C	Orthochlorophenyl-hydroxylamine	

Figure 31: Structures of Intermediate Products in OCNB Experiments

6. Comparison with Known Zinc Reductions

It is well known that the zinc reductions of nitro-aromatics yield a variety of compounds as shown in the chart below:



Since Compounds B and C are reduction products of the OCNB, it is clear that reduction as well as oxidation is occurring.

7. The Flaking Oxide Theory

Aluminum is a very reactive metal. However, unless its protective oxide coating is destroyed, aluminum is passive towards many substances. It seems probable in our experiments that insonation causes the oxide layer to flake off and expose the bare aluminum metal. Hydrogen is formed upon contact with water and a catalytic hydrogenation proceeds on the aluminum surface. Support for this comes from the fact that essentially the same products are formed on activated Raney-Nickel, which contains several percent aluminum.

8. The Temperature Rise Theory

Although no products are found in the absence of ultrasound at room temperature, reaction does occur in boiling water in 48 hours with both aluminum powder and activated Raney-Nickel. When refluxing with aluminum, however, copious quantities of $Al(OH)_3$ are formed in contrast to the room temperature sonocatalysis. While it may be possible that insonation is causing a temperature rise at the aluminum surface, the absence of $AL(OH)_3$ during sonocatalysis militates against this position.

9. Conclusions of OCNB Experiments

Sonocatalysis of aqueous OCNB over aluminum powder or

activated Raney-Nickel in the presence of air, oxygen or ozone results initially in some reduction products but eventually in oxidation products and the complete destruction of the compound. The effect of insonation may be to clean the aluminum surface by dislodging the aluminum oxide. The possibility exists that an increase in surface temperature occurs, but conditions are such that concomitant formation of $Al(OH)_3$ is prevented.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Dr. F. Patil and Dr. Konrad Seyffarth, Research Associates, for their diligent efforts and valuable contributions to this project, and to Mr. F. Y. Wound, a graduate student, for his collections of experimental data.

The financial support by the Office of Water Quality, Environmental Protection Agency, through Contract No. 14-12-572 is gratefully acknowledged. The EPA Project officer for this contract was Francis L. Evans, III. We appreciate the samples of Raney-Nickel furnished by the Davison Division of W. R. Grace and Co.

Preceding page blank

LIST OF REFERENCES

1. Bean, E.L., Advances in Chem. Ser., 21, 430 (1958).

2. Chen, J.W. and Kalback, W.M., I and EC Fundamentals, 6, 175 (1967).

3. Chen, J.W., Chang, J.A. and Smith, G.V., "Sono-Oxidation In Aqueous Solutions", Symposium Volume, "Sono Chemical Engineering," Chemical Engineering Progress, in press.

4. Currell, D.L. and Zechmeister, L., J. Amer. Chem. Soc., 80, 205-208 (1958).

5. Dixon, J.K. and Longfield, J.E., "Catalysis", Vol. VII., p. 325, Reinhold, New York (1960).

6. Fitzgerald, M., Griffing V. and Sullivan, J.J., J. Chem. Phys., 25, 926 (1960).

7. Fogler, H.S. and Barnes, D., I and EC Fundamentals, 7, 222 (1968).

8. Jellinek, H.H.G. and Whitte, G., J. Polymer Sci., 6, 6, 757-766 (1951).

9. Kilpatrick, M.L., Herrick, C.C. and Kilpatrick, M., "The Decomposition of Ozone in Aqueous Solution", J. Am. Chem. Soc., 78, 1784 (1956).

10. Koppe, P. and Giebler, G., "Ozone Decomposition in Water," Chemical Abstracts, 65, 489d (1966).

11. Lur'e, Yu Yu, Russian J. Phys. Chem., 37, No. 1, 1264 (1963).

12. Niegowski, S.J., IE & C, 45, 632 (1953).

13. Polotskii, I.G., Zhur. Obshch. Khim., 17, 649 (1947).

14. Selm, R.P., Advances in Chem. Ser., 20, (1957).

15. Torricelli, A., Advances in Chem. Ser., 21, 454 (1958).

16. Weissler, Alfred, AIChE Symposia 47, 22 (1951).

17. Zechmeister, L. and Wallcave, L., J. Amer. Chem. Soc., 77, 2953-2960 (1955).

Preceding page blank

18. Zechmeister, L. and Magoon, E.F., J. Amer. Chem. Soc., 78, 2149-2150 (1956).

19. American Public Health Association, Standard Methods for the Examination of Waste and Waste Water, 11th Ed., New York (1960).

20. Water and Waste Water Analysis Procedures, Hach Chemical Co., Ames, Iowa (1969).

21. Basic Manual of Laboratory Ozonation Techniques, The Welsbach Corporation, Philadelphia, Pa. (1970).

LIST OF PUBLICATIONS & PATENTS

1. Chen, J.W., Chang, J.A. and Smith, G.V., Symposium Series in Sono Chemical Engineering, Chemical Engineering Progress, edited by Scott Fogler, published by AIChE, New York, Vol. 67, 18-26 (1971).

2. "Sonocatalytic Processes in Advanced Waste Water Treatment," F.Y. Wound, M.S. Thesis, Southern Illinois University (1970).

3. "Sonocatalysis" by Gerard V. Smith, Juh W. Chen, F. Patil and Y. Pavlou, to be submitted to J. Catalysis.

4. "Sonocatalytic Reactions of Aqueous Orthochloronitrobenzene with Air, Oxygen and Ozone over Aluminum and Raney-Nickel During Ultrasonic Irradiation," by Gerard V. Smith, Juh W. Chen and F. Patil to be submitted to J. Catalysis.

5. "Catalytic and Sonocatalytic Oxidation of Aqueous Phenol" by Gerard V. Smith, Juh W. Chen and Konrad Seyffarth, to be submitted to J. Catalysis.

6. "Catalytic and Sonocatalytic Oxidations of Waste Waters," by Juh W. Chen, Gerard V. Smith, Konrad Seyffarth and J. Wound, to be submitted to Environmental Science and Technology.

7. Patent disclosures are being made covering the following concepts:

   a) oxidations of organic compounds in aqueous solutions using a catalyst and ozone.

   b) oxidations of organic compounds in aqueous solutions using a catalyst, ultrasound and oxygen or ozone.

   c) oxidations and/or reductions of organic compounds using aluminum or aluminum containing alloys such as Raney-Nickel in aqueous solutions and irradiating with ultrasound.

LIST OF PERSONNEL IN THE PROJECT

Dr. Juh W. Chen, Professor and Chairman, Thermal and Environmental Engineering, Coprincipal Investigator

Dr. Gerard V. Smith, Associate Professor of Chemistry, Coprincipal Investigator

Dr. F. Patil, Research Associate

Dr. Konrad Seyffarth, Research Associate

Mr. Fu-Yii Wound, Research Assistant

Preceding page blank

GLOSSARY

BOD - Biochemical Oxygen Demand

Catalyst - An agent which promotes the rate of reaction

Catalytic Oxidation - An oxidation process with catalyst and air (oxygen)

COD - Chemical Oxygen Demand

OCNB - Orthochloronitrobenzene

ODI - Oxygen Demand Index, approximately equal to BOD_5.

Sonocatalysis - Catalysis under insonation

Sonocatalytic Oxidation - Catalytic oxidation under insonation

Sonocatalytic Ozonation - Catalytic ozonation under insonation

Preceding page blank

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No. | 2. | 3. Accession No. W

4. Title: FEASIBILITY STUDIES OF APPLICATIONS OF CATALYTIC OXIDATION IN WASTEWATER,

5. Report Date

6.

7. Author(s): Chen, J. W., and Smith, G. V.

8. Performing Organization Report No.

9. Organization: Southern Illinois University at Carbondale, Ill.

10. Project No.: EPA, WQO 17020 ECI 11/71

11. Contract/Grant No.: EPA, WQO 14-12-572

12. Sponsoring Organization

13. Type of Report and Period Covered

15. Supplementary Notes

Final Contract Report, 67 p, 31 fig, 7 tab, 21 ref.

16. Abstract

Wastewaters show 78% decrease in Chemical Oxygen Demand (COD) and 96% decrease in Oxygen Demand Index (ODI) during two hours insonation in the presence of activated Raney-Nickel catalyst and air. In addition, sonocatalytic oxidation completely eliminates coliform organisms. The substitution of air by ozone-oxygen mixture can result in COD reductions of 90%. Significantly, treatment with activated Raney-Nickel and ozone, without insonation; i.e., catalytic ozonation; is nearly as effective. This process can remove 85% of the COD and 60% of the TOC from secondary treatment effluents in two hours under favorable conditions.

Ozonation of aqueous phenol solutions in the presence of activated Raney-Nickel and ultrasound (sonocatalytic ozonation) results in the reduction in phenol concentration, COD, and TOC; the greatest decrease is in phenol concentration, the next greatest is in COD, and the least is in TOC.

Aqueous solutions of Orthochloronitrobenzene (OCNB) react only in the presence of ultrasound and aluminum, or activated Raney-Nickel (sonocatalysis) at room temperature. In this reaction, reduction products appear initially, but eventually these products, and OCNB, are eliminated from the solution.

17a. Descriptors: *COD Removal, *TOC Removal, *Catalytic Oxidation of Organic Pollutants, *Catalytic Ozonation, Advanced Wastewater Treatment

17b. Identifiers: *Orthochloronitrobenzene, *Phenol, *Activated Raney-Nickel, *Ultrasound

17c. COWRR Field & Group: 05D

18. Availability

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price

Send To: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Abstractor: Juh W. Chen

Institution: Southern Illinois University